KINETIC SCHEME OF OSCILLATION REACTION OF THREE AND FOUR PARTICLES

Antonín TOCKSTEIN

Department of Physical Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

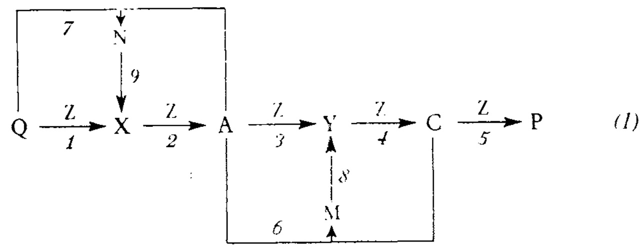
Received March 19th, 1985

The paper deals with four schemes, each of three out of the particles X, A, Y, C, consisting of two coupled autocatalytic blocks of the type $Q \rightarrow X \rightarrow A \rightarrow Y \rightarrow C$. The schemes showing relative stability of the Y particle or its dimer can exhibit a limit cycle, the other have always a stable stationary point. The scheme of four particles X, A, Y, C or dimers of particles X, Y can exhibit an unstable stationary point with the limit cycle. For the individual cases conditions were derived for the rate constants sufficient for formation of the limit cycle, and they are discussed from the point of view of available experimental data on the reaction of bromate with phenol and aniline.

In the context of studies of mechanism of the oscillation reaction between bromate and phenol[1,2] we examined[3] the kinetic scheme of reactions which were always of the 2. order and formed two autocatalytic blocks coupled by a common reaction component (Scheme 1 for k_8 and $k_9 \rightarrow \infty$). Stability of this scheme was examined[3] under the presumption that the labile intermediates X and Y are in steady state (k_2 and $k_4 \rightarrow \infty$), and for the resulting two-component scheme (A, C particles) it was shown that the particles A and C exhibit oscillations with very small damping at suitable values of the rate constants. The same result was also obtained for the three-particle scheme (A, C, X) when only the Y component was considered in steady state. As in the real system BrO_3 – phenol the X and Y particles are radicals, it seems useful to extend the scheme studied earlier by dimers of the compounds X and Y (compounds N and M in Scheme 1) and to study the behaviour and possibility of oscillations in the individual three- and four-particle schemes which is the aim of the present communication.

THEORETICAL

The basic kinetic scheme has the following form:



SCHEME 1

It would be correct to formulate most of these steps (especially *6*, *7*, *8*, *9*) as reversible, but they were considered unidirectional in order to simplify the calculations. For determination of conditions of unstability, however, this simplification represents no defect. Concentrations of the starting substances Q and Z are considered to be pseudo-constant. In the real system, Q, X, A, Y, C correspond to the bromine particles of the valence 5, 4, 3, 2, 1, respectively, Z means the organic substrate, and P stands for its bromo derivative. The corresponding kinetic equations are Eqs (*2a*–*f*) (for simplicity, both the particles and their concentrations are denoted by the same symbol).

$$\mathrm{d}X/\mathrm{d}t = k_1\, Q \,.\, Z - k_2\, X \,.\, Z + 2k_9\, N \qquad (a) \qquad (2)$$

$$\mathrm{d}N/\mathrm{d}t = k_7\, Q \,.\, A - k_9\, N \qquad (b)$$

$$\mathrm{d}A/\mathrm{d}t = k_2\, X \,.\, Z - k_7\, Q \,.\, A - k_3\, A \,.\, Z - k_6\, A \,.\, C \qquad (c)$$

$$\mathrm{d}Y/\mathrm{d}t = k_3\, A \,.\, Z - k_4\, Y \,.\, Z + 2k_8\, M \qquad (d)$$

$$\mathrm{d}M/\mathrm{d}t = k_6\, A \,.\, C - k_8\, M \qquad (e)$$

$$\mathrm{d}C/\mathrm{d}t = k_4\, Y \,.\, Z - k_6\, A \,.\, C - k_5\, C \,.\, Z \qquad (f)$$

By putting the left sides equal to zero we obtain the concentrations of the substances at the stationary point (the 0 index) as the functions of A^0: by addition of (*2c*), (*2a*), and the double of (*2b*) and addition of (*2d*), (*2f*), and the double of (*2e*), and by expressing C^0 we get (*3a*), by introducing into (*2e*) we get (*3c*), and from (*2b*) then we get (*3b*). The values (*3d*, *e*) follow

$$C^0 = \frac{k_1\, Q \,.\, Z + k_7\, Q \,.\, A^0}{k_5\, Z} \approx \frac{k_7\, Q \,.\, A^0}{k_5 Z} \qquad (a) \qquad (3)$$

$$N^0 = k_7\, Q \,.\, A^0/k_9 \qquad (b)$$

$$M^0 = k_6\, A^0\, \frac{k_1\, Q \,.\, Z + k_7\, Q \,.\, A^0}{k_8 k_5\, Z} \approx \frac{k_6 k_7\, Q \,.\, A^{0^2}}{k_8\, k_5\, Z} \qquad (c)$$

$$\mathrm{X}^0 = \frac{k_1 \mathrm{Q} \cdot \mathrm{Z} + 2k_7 \mathrm{Q} \cdot \mathrm{A}^0}{k_2 \mathrm{Z}} \approx \frac{2k_7 \mathrm{Q} \cdot \mathrm{A}^0}{k_2 \mathrm{Z}} \qquad (d)$$

$$\mathrm{Y}^0 = (k_3 \mathrm{A}^0 \cdot \mathrm{Z} + 2k_8 \mathrm{M}^0)/k_4 \mathrm{Z} \qquad (e)$$

from Eqs (*2a*) and (*2d*). The approximate expressions apply to $k_1 \to 0$.
Addition of (*2d*), (*2f*), and the double of (*2e*) gives the relation $(k_3 \mathrm{A}^0 \cdot \mathrm{Z} + k_6 \mathrm{A}^0 \cdot \mathrm{C}^0 - k_5 \mathrm{C}^0 \cdot \mathrm{Z}) = 0$ into which (*3a*) is introduced for C^0 to give a quadratic equation for A^0

$$\mathrm{A}^{0^2} k_6 k_7 \mathrm{Q} + \mathrm{A}^0(k_3 k_5 \mathrm{Z}^2 + k_1 k_6 \mathrm{Q} \cdot \mathrm{Z} - k_5 k_7 \mathrm{Q} \cdot \mathrm{Z}) - k_1 k_5 \mathrm{Q} \cdot \mathrm{Z}^2 = 0\,, \qquad (3f)$$

which for sufficiently low k_1 values leads to the simplification

$$\mathrm{A}^0 \approx (k_5 \mathrm{Z}(-k_3 \mathrm{Z} + k_7 \mathrm{Q}))/k_6 k_7 \mathrm{Q}\,. \qquad (3g)$$

The matrix* of partial derivatives of the reaction rates at the stationary point reads as follows:

$$\boldsymbol{\alpha} \equiv \begin{pmatrix} \frac{\partial \dot{\mathrm{X}}}{\partial \mathrm{X}} & \frac{\partial \dot{\mathrm{X}}}{\partial \mathrm{N}} & \cdots & \frac{\partial \dot{\mathrm{X}}}{\partial \mathrm{C}} \\ \frac{\partial \dot{\mathrm{N}}}{\partial \mathrm{X}} & \frac{\partial \dot{\mathrm{N}}}{\partial \mathrm{N}} & \cdots & \frac{\partial \dot{\mathrm{N}}}{\partial \mathrm{C}} \\ \vdots & \vdots & & \vdots \\ \frac{\partial \dot{\mathrm{C}}}{\partial \mathrm{X}} & \frac{\partial \dot{\mathrm{C}}}{\partial \mathrm{N}} & \cdots & \frac{\partial \dot{\mathrm{C}}}{\partial \mathrm{C}} \end{pmatrix} \equiv$$

$$\equiv \begin{pmatrix} -k_2 \mathrm{Z} & 2k_9 & 0 & 0 & 0 & 0 \\ 0 & -k_9 & k_7 \mathrm{Q} & 0 & 0 & 0 \\ k_2 \mathrm{Z} & 0 & \frac{-k_2 \mathrm{X}^0 \mathrm{Z}}{\mathrm{A}^0} & 0 & 0 & -k_6 \mathrm{A}^0 \\ 0 & 0 & k_3 \mathrm{Z} & -k_4 \mathrm{Z} & 2k_8 & 0 \\ 0 & 0 & k_6 \mathrm{C}^0 & 0 & -k_8 & k_6 \mathrm{A}^0 \\ 0 & 0 & -k_6 \mathrm{C}^0 & k_4 \mathrm{Z} & 0 & \frac{-k_4 \mathrm{Z}\mathrm{Y}^0}{\mathrm{C}^0} \end{pmatrix} . \qquad (4)$$

* In literature on chemical oscillations this matrix is usually denoted as community matrix which is an expression taken[4] from mathematical analysis of stability of social-economical systems.

and it is seen that conditions of qualitative instability[4] are fulfilled with the members $\alpha_{12} \cdot \alpha_{23} \cdot \alpha_{31}$, $\alpha_{36} \cdot \alpha_{63}$, $\alpha_{45} \cdot \alpha_{56} \cdot \alpha_{64}$, $\alpha_{64} \cdot \alpha_{43} \cdot \alpha_{36}$.

As the characteristical equation of the 6th order corresponding to the matrix (*4*) is much too complex for any discussion of stability, we shall restrict the discussion to examination of stability of the 3rd and 4th order equations corresponding to three- and four-particle systems. The community matrix of these simplified schemes is obtained from the matrix (*4*) by carrying out linear combination of its rows in such way that the rate constants present in kinetic products of the compounds might disappear which are omitted in Scheme 1, and also excluded are the columns corresponding to the derivatives with respect to these compounds.

Scheme of A, Y, C *Particles*

If constants k_2, k_8, k_9 of Scheme 1 are considered to be sufficiently large, then the compounds X, N, M are in steady state, and the system (*2*) is reduced to a system of three differential equations for compounds A, Y, C. The respective community matrix $\boldsymbol{\beta}$ is obtained from (*4*) by addition of the first, the double of the second, and the third rows (elimination of k_2 and k_9), and addition of the fourth and the double of the fifth rows (elimination of k_8), and by omitting the first, second, and fifth columns, the expressions for β_{11} and β_{21} being $-k_1\,QZ/A^0$ according to Eq. (*3d*) and $k_4\,Y^0Z/A^0$ according to Eqs (*2d, e*), respectively, hence the $\boldsymbol{\beta}$ matrix and the characteristical equation read as follows:

$$\boldsymbol{\beta} = \begin{pmatrix} -k_1 \dfrac{QZ}{A^0} & 0 & -k_6\,A^0 \\ k_4 \dfrac{Y^0Z}{A^0} & -k_4\,Z & 2k_6\,A^0 \\ -k_6\,C & k_4\,Z & -k_4 \dfrac{ZY^0}{C^0} \end{pmatrix}; \qquad (5a)$$

$$\begin{vmatrix} -\left(k_1 \dfrac{QZ}{A^0} + \lambda\right) & 0 & -k_6\,A^0 \\ k_4 \dfrac{Y^0Z}{A^0} & -(k_4\,Z + \lambda) & 2k_6\,A^0 \\ -k_6\,C^0 & k_4\,Z & -\left(k_4 \dfrac{ZY^0}{C^0} + \lambda\right) \end{vmatrix} = 0. \qquad (5b)$$

The $\boldsymbol{\beta}$ matrix indicates a possibility of instability due to the terms $\beta_{31} \cdot \beta_{13}$, $\beta_{23} \cdot \beta_{32}$, $\beta_{21} \cdot \beta_{13} \cdot \beta_{32}$. After development of the determinant, the characteristical equation has the form:

$$\lambda^3 + \lambda^2\left(\frac{k_1\,QZ}{A^0} + k_4\,Z\left(1 + \frac{Y^0}{C^0}\right)\right) + \lambda\left(k_4\,Z^2k_3\,\frac{A^0}{C^0} + k_4\,\frac{k_1\,QZ^2}{A^0}\left(1 + \frac{Y^0}{C^0}\right) - \right.$$

$$\left. - k_6^2A^0C^0\right) + k_4\,Z^2\left(k_1\,\frac{QZ}{C^0}\,k_3 + k_5k_6\,C^0\right) \equiv \lambda^3 + a_1\lambda^2 + a_2\lambda + a_3 = 0\,, \quad (5c)$$

the relations $k_4\,ZY^0/C^0 - 2k_6\,A^0 = k_3\,A^0Z/C^0$ (following from Eqs (*2d, e*)) and $k_4\,Y^0Z - k_6\,A^0C^0 = k_5\,C^0Z$ (from Eq. (*2f*)) being used in its modification.

According to the Hurwitz criterion[8], the necessary and sufficient condition of stability of a stationary point is given by the requirements:

$$a_1 > 0\,; \quad a_1a_2 - a_3 > 0\,; \quad a_3(a_1a_2 - a_3) > 0\,. \qquad (6a, b, c)$$

A breach of any of the conditions (*6a, b, c*) results in instability of the stationary point and, hence, in explosion or in oscillations. As the a_1 and a_3 coefficients are always positive, the condition (*6b*) can only be broken; then (*6c*) is broken automatically. However, the whole relation $a_1a_2 < a_3$ is much too complex for discussion, so we shall restrict it to the sufficient condition, *i.e.* $a_2 \leqq 0$, even though the possible unstability region is thereby somewhat reduced. Hence the sufficient condition of instability reads as follows:

$$k_4\,\frac{k_1\,QZ^2}{A^0}\left(1 + \frac{Y^0}{C^0}\right) + k_3k_4\,Z^2\,\frac{A^0}{C^0} - k_6^2\,A^0C^0 \leqq 0 \qquad (7a)$$

and it implicates one negative root λ and two positive and/or complex roots with real part. For sufficiently low k_1 values it can be transformed into Eq. (*7b*) by factoring out A^0/C^0 and introducing (*3a*).

$$Z(\sqrt{(k_3k_4)} + k_3) < k_7\,Q \qquad (7b)$$

If the system of the A, Y, C particles should exhibit unstability, it is necessary according to the relation (*7b*) that the k_3 and k_4 constants were not too large and k_7 too small. If the relation (*7b*) is fulfilled, the trajectory exhibits a limit cycle whose A–C and Y–C trajectories are very similar in shape to the A–C and M–C trajectories (Fig. 1). Magnitude of the limit cycle and of the amplitude of concentrations increase with increasing k_7 and k_5 and with decreasing k_3, k_4, k_6, which was found by an analogue computer.

For $k_4 \to \infty$ the stationary point becomes stable, and the scheme is transformed into a two-particle one (A, C), and the λ_1, λ_2 roots have negative real part with the discriminant[3]

$$D = \left(\frac{k_1 Q}{A^0} - \frac{k_3 A^0}{C^0}\right)^2 - 4k_6k_5\frac{C^0}{Z}, \qquad (8a)$$

which secures damped oscillations of the concentrations of A, C for $D < 0$ and a monotonous course for $D > 0$.

Hence by increasing k_4, *i.e.* by decreasing the stability of the intermediate Y, it is possible to change from the undamped oscillations to the damped ones or to monotonous course of the concentrations depending on the D value. If the limit cycle is to be changed (by increasing k_4) into a stationary point without rotational trajectories of spiral shape, i.e. from the non-damped oscillations directly to the monotonous course and *vice versa*, then it is necessary (according to (*8a*) and (*7b*)) that the relations (*8b, c*) were simultaneously fulfilled on the limit cycle (for $k_1 \rightarrow 0$):

$$(k_3k_5 Z/k_7 Q)^2 > 4k_5(k_7 Q/Z - k_3), \qquad (8b)$$

$$(k_3k_4)^{1/2} < k_7 Q/Z - k_3. \qquad (8c)$$

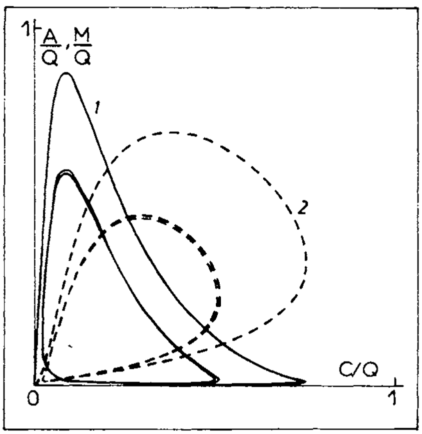


FIG. 1

The limit cycle of A, M, C particles. The trajectories of relative concentrations: *1* phase plane A—C, *2* phase plane M—C. The solution by means of the analogue computer for chosen rate constants: $k_1 = 10^{-2}$; $k_3 = 7\cdot8 \,.\, 10^{-2}$; $k_5 = 88\cdot1 \,.\, 10^{-2}$; $k_6n = 6\cdot72$; $k_7n = 0\cdot673$; $k_8/Z = 0\cdot844$; $k_{10} = 0\cdot133$

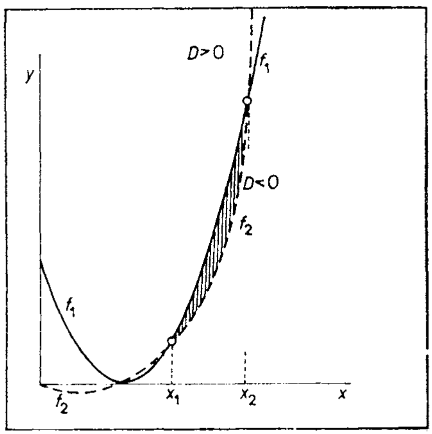


FIG. 2

Scheme of delimitation of stability and non-stability region of stationary point in the scheme of A, Y, C particles. The dashed line denotes the f_2 function with $D = 0$; the heavy line denotes the f_1 function forming the boundary of non-stability

If we denote $k_7\,Q/k_3\,Z = x$, $k_5/k_3 = y$, $(k_4/k_5)^{1/2} = u$, then the relations (*8b, c*) are fulfilled for the points whose positive coordinates $x - 1, y, u$ lie outside the body given by the surface $y = ((x - 1)/u)^2 = f_1(x, u)$ and inside the body given by the surface $y = 4x^2(x - 1) = f_2(x, u)$, hence, for an u chosen as a parameter there must exist real points of intersection of the curves f_1 and f_2, which necessitates $16u^2 < 1$, *i.e.* $k_4 < k_5/16$. At a chosen u value these are points lying in the region determined by the two curves and points of intersection $x_{1,2} = [1 \pm \sqrt{(1 - 16u^2)}]/ /8u^2$ (see the vertically hatched area in Fig. 2).

Scheme of A, M, C *Particles*

If constants k_2, k_4, k_9 of Scheme 1 are considered to be sufficiently large, then the compounds X, Y, N are in steady state, and the system (*2*) is reduced to a system of three differential equations for the compounds A, M, C. The corresponding community matrix γ is obtained from (*4*) by addition of the first and the third rows and the double of the second row (elimination of k_2 and k_9) and by addition of the rows 4 and 6 (elimination of k_4) in the form ($\gamma_{11} = -k_1\,QZ/A^0$):

$$\gamma = \begin{pmatrix} k_7\,Q - k_3\,Z - k_6\,C^0 & 0 & -k_6\,A^0 \\ k_6\,C^0 & -k_8 & k_6\,A^0 \\ k_3\,Z - k_6\,C^0 & 2k_8 & -(k_6\,A^0 + k_5\,Z) \end{pmatrix}. \tag{9}$$

And the characteristical equation reads as follows:

$$\begin{vmatrix} -\left(\dfrac{k_1\,QZ}{A^0} + \lambda\right) & 0 & -k_6\,A^0 \\ k_6\,C^0 & -(k_8 + \lambda) & k_6\,A^0 \\ k_3\,Z - k_6\,C^0 & 2k_8 & -(k_6\,A^0 + k_5\,Z + \lambda) \end{vmatrix} = 0\,. \tag{10a}$$

The γ matrix indicates a possibility of instability due to the members $\gamma_{32} \cdot \gamma_{23}$, $\gamma_{13} \cdot \gamma_{31}$, and $\gamma_{21} \cdot \gamma_{13} \cdot \gamma_{32}$. After development of the determinant, the characteristical equation has the following form:

$$\begin{aligned} &\lambda^3 + \lambda^2(k_1\,QZ/A^0 + k_5\,Z + k_6\,A^0 + k_8) + \lambda(k_8(k_5\,Z - k_6\,A^0) + \\ &+ (k_1\,QZ/A^0)(k_6\,A^0 + k_5\,Z + k_8) + k_6\,A^0(k_3\,Z - k_6\,C^0)) + \\ &+ k_6k_8\,A^0(k_3\,Z + k_6\,C^0) + (k_1\,QZ/A^0)\,k_8(k_5\,Z - k_6\,A^0) = 0\,. \end{aligned} \tag{10b}$$

A sufficient condition of instability of the stationary point is a negative or zero value of the coefficient at $\boldsymbol{\lambda}$, *i.e.*

$$k_8k_5\,\mathrm{Z} - k_8k_6\,\mathrm{A}^0 + k_1\,\mathrm{QZ}(k_6 + (k_5\,\mathrm{Z} + k_8)/\mathrm{A}^0) + k_3k_6\,\mathrm{A}^0\mathrm{Z} - k_6^2\,\mathrm{A}^0\mathrm{C}^0 \leqq 0\,, \tag{11a}$$

which can be modified by introducing *(3g)* for A^0 and the simplified equation *(3a)* for C^0 to give the form ($n = Q/Z$):

$$3 + k_8/k_7\,\mathrm{Q} + \delta \leqq nk_7/k_3 + 2k_3/nk_7$$
$$\delta = (nk_1k_6/k_3k_5)(1 + k_7n/(k_7n - k_3) + (1 + k_8/k_5\,\mathrm{Z}))\,. \tag{11b}$$

Small values of the rate constants k_1, k_3, k_6, k_8 and large values of the constants k_5, k_7 and of the n parameter contribute to fulfilling of this inequality, *i.e.* to formation of instable stationary point. If Eq. *(11b)* is fulfilled, then there exits a limit cycle (Fig. 1). A solution by means of an analogue computer showed that magnitude of the limit cycle and of the amplitude of concentrations of the particles A, M, C are increased with decreasing k_3, k_6, k_8, k_{10} and with increasing k_5 and k_7. Decreasing k_3 and increasing k_7 result in making more distinct the concave character of the A–C curve when going from the maximum A to the maximum C; decreasing k_6 makes more distinct the concave character and decreases the slope of the M–C curve in the region of its increase at small values of M and C; the decrease in k_8 has the opposite effect.

So far the existence of the limit cycle in the scheme of A, M, C particles has been proved[5] by reduction to the two-particle scheme (A, M) with the presumption $\mathrm{d}C/\mathrm{d}t = 0$.

For $k_8 \to \infty$ the scheme changes into a stable two-particle scheme of compounds A, C. If the increase in k_8 has to change the limit cycle into stable stationary point without rotational trajectories, then according to *(11b)* and *(8a)* the inequalities *(8b)* and *(11c)* must be fulfilled on the limit cycle (for $k_1 \to 0$):

$$3 + k_8/k_7\,\mathrm{Q} < k_7\,\mathrm{Q}/k_3\,\mathrm{Z} + 2k_3\,\mathrm{Z}/k_7\,\mathrm{Q}\,. \tag{11c}$$

If we denote $k_7\,\mathrm{Q}/k_3\,\mathrm{Z} = x$, $k_5/k_3 = y$, $k_8/k_5\,\mathrm{Z} = v$, then the inequalities *(8b)*, *(11c)* are fulfilled for the points with positive coordinates $x - 2$, y, v lying inside the body given by the surface $y = 4x^2(x - 1) \equiv f_2(x, v)$ and outside the body given by the surface $4y = (x - 2)(x - 1)/v \equiv f_3(x, v)$. For a v chosen as a parameter there must exist real points of intersection of the curves f_2, f_3, which necessitates that $1 > 32\,v$, *i.e.* $k_8 < k_5\,\mathrm{Z}/32$. The points fulfilling the inequalities *(8b)*, *(11c)* lie – for the v chosen – in the region determined by the two curves f_1, f_2 and the points of intersection $x_{1,2} = (1 \pm (1 - 32\,v)^{1/2})/8\,v$ (see the vertically hatched area in Fig. 3). If Scheme 1 is extended by the step *10* in the form $\mathrm{M} + \mathrm{Z} \xrightarrow{k_{10}} 2\,\mathrm{C}$

proceeding in parallel way to the step *8*, then the results obtained remain valid, only it is necessary to replace the k_8 constant by the sum $k_8 + k_{10}$ Z.

Scheme of X, A, C *Particles*

This scheme is formed from Scheme 1 for high values of k_4, k_8, k_9, and it was shown in the previous work[3] that its stationary point is always stable, and the scheme can exhibit slowly damped oscillations at the most.

Scheme of N, A, C *Particles*

This scheme is formed from the previous one, if $k_2 \to \infty$ but k_9 is sufficiently small. The corresponding community matrix ϑ is given by Eq. (*12a*), and the characteristical equation, after development of the determinant, has the shape of Eq. (*12b*).

$$\vartheta = \begin{pmatrix} -k_9 & k_7 \mathrm{Q} & 0 \\ 2k_9 & -(k_1 \mathrm{QZ} + 2k_9 \mathrm{N}^0)/\mathrm{A}^0 & -k_6 \mathrm{A}^0 \\ 0 & k_5 \mathrm{CZ}/\mathrm{A}^0 & -k_3 \mathrm{A}^0\mathrm{Z}/\mathrm{C}^0 \end{pmatrix} \qquad (12a)$$

$$\lambda^3 + \lambda^2(k_9 + 2k_7 \mathrm{Q} + k_3 \mathrm{A}^0\mathrm{Z}/\mathrm{C}^0 + k_1 \mathrm{QZ}/\mathrm{A}^0) + + \lambda((k_3 \mathrm{A}^0\mathrm{Z}/\mathrm{C}^0)(k_1 \mathrm{QZ}/\mathrm{A}^0 + 2k_7 \mathrm{Q}) + k_5k_6 \mathrm{C}^0\mathrm{Z} + + k_9(k_3 \mathrm{A}^0\mathrm{Z}/\mathrm{C}^0 + k_1 \mathrm{QZ}/\mathrm{A}^0)) + k_9(k_3k_1 \mathrm{QZ}/\mathrm{C}^0 + k_5k_6 \mathrm{C}^0\mathrm{Z}) = 0 \qquad (12b)$$

Although the ϑ matrix indicates a possibility of instability with the term $\vartheta_{21} \cdot \vartheta_{12}$, the Hurwitz's necessary and sufficient condition of stability $a_1a_2 - a_3 > 0$ is ful-

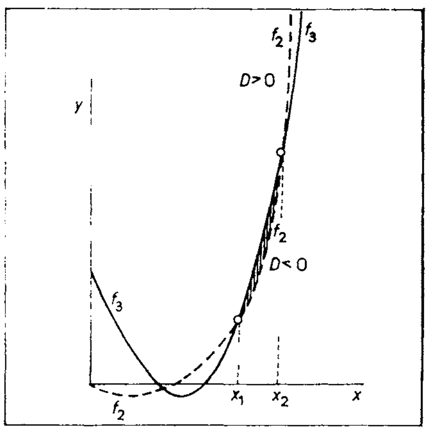


FIG. 3
Scheme of delimitation of stability and non--stability region of stationary point in the scheme of A, M, C particles. The graphical symbols have similar meaning as those in Fig. 1

filled always here, so the scheme of N, A, C particles cannot lead to undamped oscillations.

Four-Particle Scheme of Compounds N, A, M, C

For k_2, $k_4 \to \infty$ and steady states for compounds X and Y the matrix (*4*) is transformed into a matrix which has the characteristical equation (*13a*) whose development leads to an equation of the 4th order.

$$\begin{vmatrix} -(k_9 + \lambda) & k_7 \mathrm{Q} & 0 & 0 \\ 2k_9 & -(k_7 \mathrm{Q} + k_6 \mathrm{C}^0 + k_3 \mathrm{Z} + \lambda) & 0 & -k_6 \mathrm{A}^0 \\ 0 & k_6 \mathrm{C}^0 & -(k_8 + \lambda) & k_6 \mathrm{A}^0 \\ 0 & k_3 \mathrm{Z} - k_6 \mathrm{C}^0 & 2k_8 & -(k_6 \mathrm{A}^0 + k_5 \mathrm{Z} + \lambda) \end{vmatrix} = 0 \qquad (13a)$$

In the approximation of $k_1 \to 0$, the sum $k_7 \mathrm{Q} + k_6 \mathrm{C}^0 + k_3 \mathrm{Z} = (k_1 \mathrm{QZ} + k_9 \mathrm{N}^0)/\mathrm{A}^0$ can be replaced by the expression $2k_7 \mathrm{Q}$, and the sum $k_3 \mathrm{Z} + k_6 \mathrm{C}^0$ can be replaced by the expression $-k_5 \mathrm{C}^0\mathrm{Z}/\mathrm{A}^0$, so after development of the determinant, the characteristical equation in the mentioned approximation reads as follows:

$$\lambda^4 + \lambda^3(k_5 \mathrm{Z} + k_6 \mathrm{A}^0 + k_8 + k_9 + 2k_7 \mathrm{Q}) + \lambda^2(k_8k_3 \mathrm{A}^0\mathrm{Z}/\mathrm{C}^0 + (k_5 \mathrm{Z} + k_6 \mathrm{A}^0 + k_8)(k_9 + 2k_7 \mathrm{Q}) + k_6 \mathrm{A}^0(k_3 \mathrm{Z} - k_6 \mathrm{C}^0)) + \lambda((k_8k_3 \mathrm{A}^0\mathrm{Z}/\mathrm{C}^0)(k_9 + 2k_7 \mathrm{Q}) + k_5k_6k_8 \mathrm{C}^0\mathrm{Z} + k_9k_6 \mathrm{A}^0(k_3 \mathrm{Z} - k_6 \mathrm{C}^0)) + k_5k_6k_8k_9 \mathrm{C}^0\mathrm{Z} = 0 \,. \qquad (13b)$$

For $k_9 \to \infty$ Eq. (*13b*) is reduced to (*10b*), for $k_8 \to \infty$ Eq. (*13b*) changes to (*12b*), and for simultaneous k_8, $k_9 \to \infty$ it gives the relation (*5a*) in the previous communication[3], in all three cases, of course, in the approximation $k_1 \to 0$. The Hurwitz conditions[8] of stability of a polynomial of the 4th order are gviven in (*14a, b, c, d*).

$$a_1 > 0\,; \quad a_1a_2 - a_3 > 0\,; \quad a_1(a_2a_3 - a_1a_4) - a_3^2 > 0\,; \quad a_4(a_1(a_2a_3 - a_1a_4) - a_3^2) > 0 \qquad (14a, b, c, d)$$

Comparison with (*13b*) shows that only a_2 or a_3 could be negative and, hence, could break (with a_1 and a_4 positive) the conditions (*14b, c, d*) or (*14c, d*) for $a_2 \leqq 0$ or $a_3 \leqq 0$, respectively. But introduction for A^0, C^0 into a_2 and a_3 shows that a_2 is always positive, whereas a_3 can become negative, so that the only sufficient condition for formation of unstable stationary point is $a_3 \leqq 0$, and it can be modified into the form:

$$k_8/k_7 Q + (k_8/k_9)(1 + k_7 Q/k_8 Z) + 3 < k_7 Q/k_8 Z + 2k_3 Z/k_7 Q \qquad (15)$$

which represents a generalization of the condition (*11c*), and it can be seen that a low k_9 value, *i.e.* relative stability of the N particle, acts against formation of the limit cycle.

An interesting result is obtained, if not only the step 8 is extended by the parallel reaction $M + Z \xrightarrow{k_{10}} 2\,C$, but also the step 9 is extended by the parallel reaction $N + Z \xrightarrow{k_{11}} 2\,A$. Then the previous results remain valid, but k_8 and k_9 must be replaced by the sums

$$k'_8 = k_8 + Zk_{10}\,, \quad k'_9 = k_9 + Zk_{11}\,. \qquad (16a, b)$$

The relation (*15*) with the sign of equality represents – at a chosen constant ratio $W = k_7 Q/k_3 Z$ – equation of the surface $(k'_8 k'_9 Z)$ which, together with the plane $k'_8 = 0$, represents the space in which the inequality (*15*) is fulfilled. The relations (*16a, b*) represent equation of straight line in the same coordinates. If this straight line has two positive real points of intersection with the plane (Fig. 4), then the region between them represents the k'_8, k'_9, Z values for which the inequality (*15*) is fulfilled and, hence, there exist an unstable stationary point and the limit cycle. Before and after this region the stationary point is stable. This means that at suitable values of the rate constants (Eq. (*17*)) the reaction can exhibit a non-oscillating course in sufficiently diluted solutions ($Z \approx 0$), then there exists a region of non-damped oscillations at the increased concentration Z (at constant W), and the non-damped oscillations again disappear on further increasing the Z concentration.

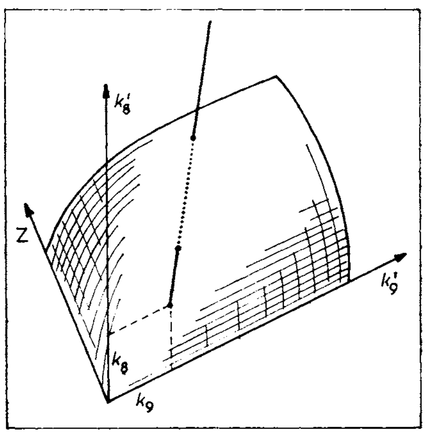


FIG. 4
The surface $(k'_8 k'_9 Z)$ and straight line $(k'_8(Z), k'_9(Z))$

The requirement of the existence of two real positive points of intersection of the straight line (*16a, b*) and the surface ($k'_8 k'_9$ Z) necessitates that the quadratic equation for Z

$$Z^2(k_{10}(k_{11}W^{-1} + k_3(1 + W)) - k_3k_{11}(W + 2W^{-1} - 3)) + \\ + Z(k_8(k_{11}W^{-1} + k_3(1 + W)) + k_9k_{10}W^{-1} - k_3k_9(W + 2W^{-1} - 3)) + \\ + k_8k_9W^{-1} = 0 \tag{17}$$

had two positive real roots. For considerably high W values, the absolute term of Eq. (*17*) is negligible, so that one root is $Z_1 \approx 0$, and the other is $Z_2 \approx -(k_8 - k_9)/ /(k_{10} - k_{11})$, which requires $k_8 < k_9$ or $k_{10} < k_{11}$.

Four-Particle Scheme of Compounds X, A, Y, C

For $k_8, k_9 \rightarrow \infty$ the matrix (*4*) gives the characteristical equation

$$\begin{vmatrix} -(k_2 Z + \lambda) & 2k_7 Q & 0 & 0 \\ k_2 Z & -(k_2 X^0Z/A^0 + \lambda) & 0 & -k_6 A^0 \\ 0 & k_4 Y^0Z/A^0 & -(k_4 Z + \lambda) & 2k_6 A^0 \\ 0 & -k_6 C^0 & k_4 Z & -(k_4 Y^0Z/C^0 + \lambda) \end{vmatrix} = 0 \tag{18a}$$

which on development of the determinant and modification reads as follows (in the approximation $k_1 \rightarrow 0$):

$$\lambda^4 + \lambda^3(k_4 Z(1 + Y^0/C^0) + k_2 Z + 2k_7 Q) + \lambda^2(k_4 Z(k_3 A^0Z/C^0 + \\ + (1 + Y^0/C^0)(k_2 Z + 2k_7 Q)) - k_6^2 A^0C^0) + \\ + \lambda((k_3k_4 A^0Z/C^0)(k_2 Z + 2k_7 Q) + k_4k_5k_6 C^0Z^2 - k_2 Zk_6^2 A^0C^0) + \\ + k_2 Zk_4k_5k_6 C^0Z^2 = 0 . \tag{18b}$$

For $k_2 \rightarrow \infty$ and $k_4 \rightarrow \infty$ it is reduced to Eqs (*5b*) and (*7a*) of ref.[3], respectively, both in the approximation $k_1 \rightarrow 0$. The sufficient condition of unstability, *i.e.* $a_2 \leqq 0$ or $a_3 \leqq 0$, again can be fulfilled here only for $a_3 \leqq 0$ (a_2 being always positive after introduction for Y^0, C^0, A^0), and modification gives the relation (*19*) which represents an extension of (*7b*)

$$k_3k_4 Z^2(1 + 2k_7 Q/k_2 Z) + (k_4 Zk_7 Q/k_2 Z)(k_7 Q - k_3 Z) < (k_7 Q - k_3 Z)^2 \tag{19}$$

and indicates that relative stability of the intermediate X acts against formation of unstable stationary point.

DISCUSSION

Comparison of behaviour of the two-particle scheme A, C with the three-particle ones A, Y, C or A, M, C or with the four-particle ones X, A, Y, C or N, A, M, C shows that a sufficient stability of the third particle Y or M and high unstability of the particle X or N enable formation of unstable stationary point and, hence, the existence of non-damped oscillations even in such cases where the two-particle scheme (A, C) itself would have positive discriminant and, hence, non-oscillating solution due to unfavourable values of k_1, k_3, k_5, k_7 constants (Eq. (*8a*)).

In real systems where the individual types of intermediates acting as the substrate Z can be changed in the course of the reaction (due *e.g.* to substitution – bromination) the individual rate constants of the steps *1, 3, 4, 5, 10* (involving the substrate) can be changed in the course of the reaction. Decrease of k_1, k_3, k_4, k_{10} and increase of k_5 can cause fulfilling of the inequality (*11b*) or (*7b*) and thus formation of the limit cycle, *i.e.* non-damped oscillations starting from a certain moment in the reaction course (Fig. 5). This represents finishing of the induction period which is of another type than that of the mechanisms necessitating only accumulation of some of the intermediates (*e.g.* Br^- in Oregonator[6]) without any change of rate constants of the individual steps during the reaction.

A decision between the two alternatives of evocation of the limit cycle by action of the substrate (*1.* lowering of the constants in the group k_1, k_3, k_4, k_{10}; *2.* increase of k_5) is enabled by the following consideration: in the second alternative the substitution products of the original substrate react faster than the starting compound Z which thus remains in the reaction mixture until the end of the reaction. In the opposite case the starting substance Z is consumed preferably so that it disappears

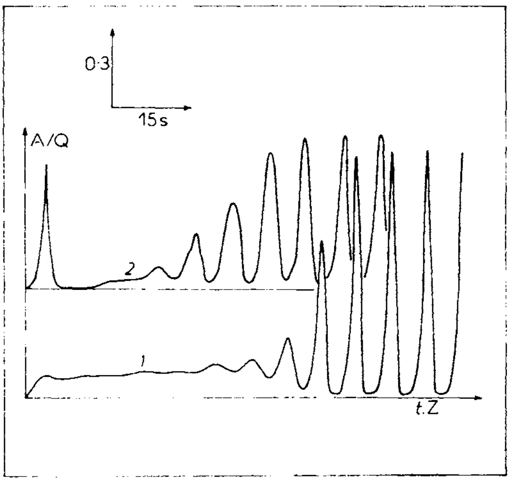


FIG. 5

The induction period and development of non-damped oscillations. The solution by means of the analogue computer in the coordinates relative concentration A/Q – generalized time *t*.Z with the constants: $k_1 = 10^{-2}$, $k_6n = 6{\cdot}72$; $k_7n = 0{\cdot}673$; $k_8/Z = 0{\cdot}844$; $k_{10} = 0{\cdot}133$. *1*: $k_5 = 0{\cdot}881$, k_3 was continuously changed from the value 0·6 to 0·049 during the induction period. *2*: $k_3 = 0{\cdot}078$, k_5 was continuously changed from the value 0·2 to 0·881 during the induction period at the end of the induction period, and evocation of oscillations must be due to lowering of the constants of the first group. This also means that an addition of the original substrate Z to the oscillating reaction mixture will suppress the oscillations in the first alternative (increase of the constants of the first group), whereas it has no effect in the second alternative. An addition of the substitution products of the original substrate to the oscillating mixture has no effect in the first alternative, whereas in the second alternative it can suppress the oscillations (if besides k_5 also the constants of the first group are increased). Moreover, from the above-mentioned consideration it follows that application of the substrate already substituted (as the starting substance) can evoke oscillation and shorten the induction period in the first alternative, whereas in the second alternative these results need not be observed.

Experimental findings about reaction of bromate with aniline[7] or phenol[1,2] agree fully with the prognoses described and indicate that aniline and phenol obey the second and the first alternatives, respectively.

In the scheme of A, M, C particles the dilution effect also makes itself felt on the existence of the limit cycle. If the kinetic equations are written in relative concentration and in the generalized time, then the initial concentration of the substrate Z has no effect on the above-mentioned quantities except k_8/Z which increases with dilution. At a sufficiently large dilution the limit cycle (*i.e.* the non-damped oscillations) disappears. Such behaviour was also observed in the reactions of phenol[1,2] and aniline[7] with bromate. The scheme of N, A, M, C particles even shows an only limited region of dilution in which the non-damped oscillations are possible, as it was shown in connection with Eq. (*17*).

The results given indicate that Scheme 1 can be considered a suitable basis for further investigation of the oscillation reactions of bromate with aromatic substrates.

REFERENCES

1. Tockstein A., Handlířová M.: This Journal *47*, 2454 (1982).
2. Tockstein A., Handlířová M.: *Kinetics of Physicochemical Oscillations*, Vol. I, p. 142. Aachen 1979.
3. Tockstein A., Komers K.: This Journal *45*, 2135 (1980).
5. Tyson J. J.: J. Chem. Phys. *62*, 1010 (1975).
5. Noszticzius Z., Farkas H.: Springer Ser. Chem. Phys. *18*, 275 (1981).
6. Field R., Noyes R. M.: J. Chem. Phys. *60*, 1877 (1974).
7. Handlířová M., Tockstein A.: Unpublished results.
8. Schwarz Š.: *Základy náuky o riešení rovníc*. Publishing House of Slovak Academy of Sciences, Bratislava 1967.

Translated by J. Panchartek.