

Electronic Supplementary Information

Oscillatory behavior of the surface reduction process of multilayer graphene oxide at room temperature

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Experimental Details

Chemicals

Graphite powder of brand HA-1 was used. H₂SO₄ (99.9%) and HCl (36%) were purchased from Sigma-Aldrich Tech; HNO₃ (65%) and K₂MnO₄ (chemically pure) were obtained from Chimmed, Russia. Twice distilled water was used in sample preparation.

Synthesis of GO

Graphite (20 g) and concentrated H₂SO₄ (600 mL) were placed in a three necked 2 L flask equipped with a mechanical stirrer and a thermometer. Concentrated HNO₃ (10 mL) was added with stirring and the mixture was heated by a water bath (45 °C) until the blue-colored graphite bisulfate appeared. The mixture was cooled to 10-15 °C and KMnO₄ (60 g) was added in portions over a period of 1 h. the temperature being maintained below 20 °C. After the addition had been completed, the mixture was slowly cooled with stirring to 4 °C and left overnight. Then the mixture was cooled again to 10-15 °C and 1 L of water was added in portions with continuous stirring and the temperature being maintained below 50 °C. The resulting suspension was poured into a 3 L beaker and concentrated H₂O₂ (50 mL) was slowly (due to foaming) added with stirring. The warm mixture was centrifuged, the precipitate was separated and suspended in 1 L of 3% HCl and the suspension was centrifuged. The procedure was repeated 4-5 times. Then GO was diluted with water to 25 L and washed with decanting until the pH of the wash water was >4.0 and SO₄²⁻ or Cl⁻ ions were not detected. After the preparation, water solution of GO was centrifuged for 5 min at 800G. The resulting solution was transparent and had a slight brown color.

Experimental techniques and sample preparation

The GO films were prepared from centrifuged GO water solution by consecutive drop casting on a Teflon film to avoid adhesion. Before drop casting Teflon supports were cleaned by polar (THF) and non-polar (hexane) solvents in ultrasound bath. The typical thickness of GO film for XPS measurements was about 1 micron which means hundreds of single flakes of multilayer GO.

XPS was performed using ESCA with Phoibos-150 analyzer (SPECS, Germany). A non-monochromatized MgK α X-ray source was used ($h\nu = 1253.6$ eV), that penetrates approximately

the top 40 Å of the film. All the XPS signals were recorded with a pass energy equal to 30 eV. The pressure in the sample chamber did not exceed 8×10^{-10} Torr. The scanning condition for all measurements was as follows: 100 ms/step, 0.1-0.05 eV/step and 30 sweeps. We should note that samples were stored in the XPS vacuum chamber during the all days of experiment.

Fitting of the XPS data were done using CasaXPS 2.3.16Dev.52 software with Marquardt's iteration method. For our data, the Tougaard background type was used and all curves were defined as 20% Lorentzian, 80% Gaussian (same way as it was performed in Ref. ²). The spectra of initial GO film revealed electrostatic charging. Since we used the same material to prepare all GO film it is obvious to expect the same average value of binding energies for "C-C" electrons. We obtained this value (284.6 eV) based on experimental results of thermally reduced GO. Thus, charging shift was corrected for all spectra in CasaXPS program using the Calibration utility.

SPM measurements were performed using Scanning Probe Nanolaboratory Integra Aura (NT-MDT, Russia). We used three types of tips: standard silicon tips with curvature radius about 10 nm and supersharp DLC tips with curvature radius about 1 nm for studying topology in tapping mode (all NT-MDT, Russia). SKPM measurements were performed under low vacuum (about 50 mbar) using standard tips covered by PtIr (curvature radius \sim 20 nm) with a WF \sim 5.2 eV, which were previously calibrated by measurements of fresh cleaved HOPG surface with a stable value of WF = 4.6 eV. For scanning Kelvin probe microscopy measurements, an AC voltage with an amplitude of $V_{AC} = 0.2$ V at a frequency of $f = 154.657$ kHz was applied to a probe. It should be noted that during all tapping-mode and SKPM measurements amplitude of the tip deviation was about 4 nm.

For SPM measurements samples of initial GO were prepared by following steps. A solution with a volume of 10 μ l was drop-casted onto a substrate and after 1 minute was absorbed by filter paper (without touching the surface). For positive GO sheet identification the following operations were performed: a fresh flake of HOPG attached to the pyroceramic substrate with bi-adhesive tape, was placed on the scanner with a maximum scanning range of 100 microns. In the beginning, a number of measurements detected displacement of the substrate due to the reverse deformation of the bi-adhesive tape. As a result, the sample was left untouched for the day then was scanned again. This procedure was performed until the displacement was within acceptable bounds (not more than 20 nm/15 min).

Raman measurements were performed in the backscattering geometry using a Jobin Yvon T64000 triple monochromator spectrometer. Coherent Verdi II solid state laser with the wavelength of 532 nm was used. The laser power on the sample was 0.5 mW.

Comments for XPS results

The result of additional measurements of 8 different samples is presented on the Figure S1a. We should note that found results depended on the time elapsed from GO deposition moment (t_d). On the Figure S1 b kinetic behavior of "C-C" maximum after normalization on t_d is presented.

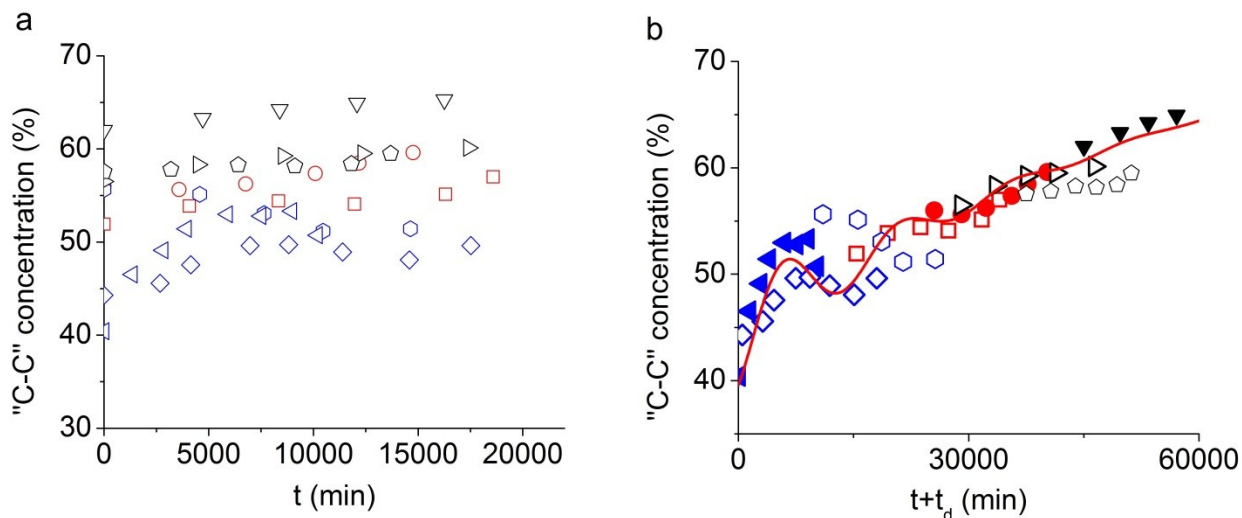


Figure S1. a. The time dependence of “C-C” concentration of eight samples, **b.** The same time dependences of C-C concentration on time of experiment accounting t_d - time elapsed from the GO film deposition moment. Red curve is fitting result obtained for the data on the Figure 6 (main article) using “reactive edges model”.

Deconvolution procedure

The deconvolution procedure is the one of tricky aspects of XPS analysis. While the first maximum at 284.6 eV is well defined and obviously assigned to electrons from the carbon atoms bonded with another carbon or hydrogen (“C-C” maximum), the next pronounced maximum at about 287 eV may consist of several peaks. Originally, this peak corresponds to electrons from carbon atoms, which are chemically bonded with oxygen by single bond (“C-O”). According to various sources (See, for example, Ref.³), the position of the hydroxyl and epoxide/ether groups on the XPS spectrum differs by about 0.5 - 1.1 eV. At conditions of visual indistinguishability of second maximum components, a lack of desire to speculate seems quite correct. Description of the second maximum with several peaks should be subject to the principles of expediency. In our experiments, the reason for approximation of second maximum by two functions was the observed change in its position relative to the normalized “C-C” peak. The distance between the “C-O” and “C-C” maxima changes by about 0.4 eV (Figure S2).

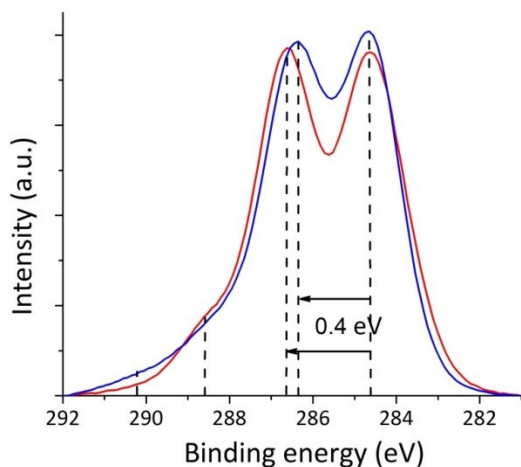


Figure S2. C1s spectra of GO at different time, when the shift of the second peak was maximal.

This shift cannot be explained by relaxation phenomena also, since in this case peak position should shift to higher binding energies and coincide with charging shift, what was not observed (Figure S3). The only reasonable explanation for this effect is the changes of ratio between the signals from electrons of carbon in epoxy and hydroxyl groups due to the variation of their concentrations.

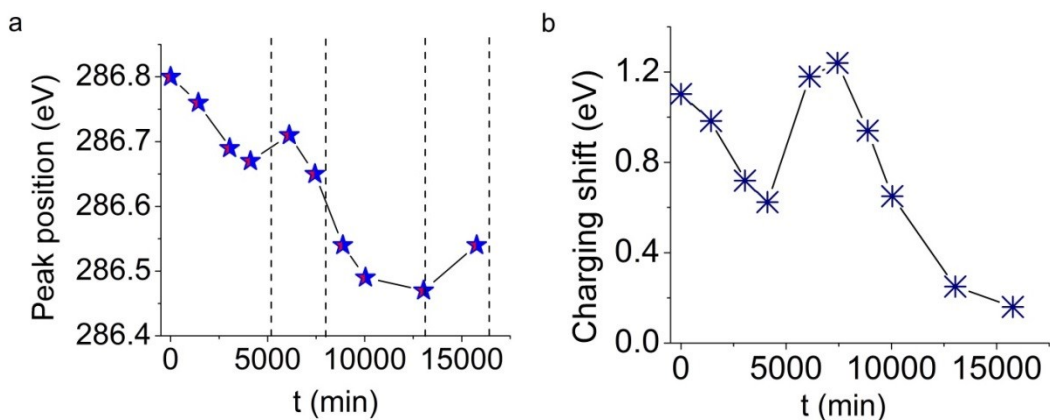


Figure S3. The dependences of “C-O” peak position and charging shift on time.

We should note that oscillatory-like behavior of “C-C” and “C-O” components did not depend on how many functions (three or five) we used. The time dependence of concentration “C-C” and “C-O” components is shown on the Figure S4.

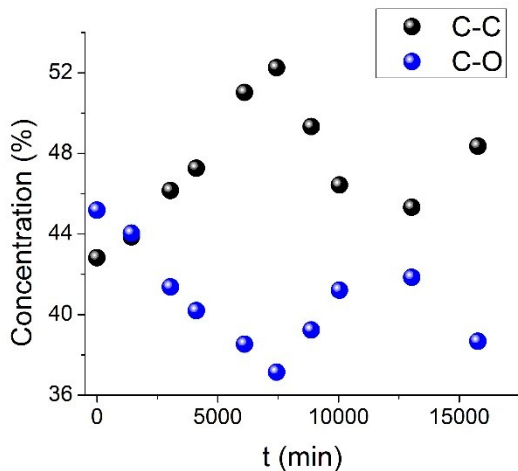


Figure S4. The time dependence of concentration “C-C” and “C-O” components at three function deconvolution procedure.

Comments on theoretical models

Reactive edges model

We analyzed the following chemical reactions:

- 1) $(O_2) + 2\{Z\} \rightleftharpoons 2\{ZO\}$,
- 2) $(H_2) + 2\{Z\} \rightleftharpoons 2\{ZH\}$,
- 3) $\{ZO\} + \{ZH\} \rightleftharpoons \{Z\} + \{ZOH\}$,
- 4) $\{ZOH\} + \{ZH\} \rightarrow 2\{Z\} + (H_2O)$,
- 5) $(H_2O) + \{Z\} \rightleftharpoons ZH_2O$,
- 6) $(H_2) + \{Z\} \rightleftharpoons \{ZH_2\}$,
- 7) $\{ZH_2\} + \{ZO\} \rightarrow 2\{Z\} + (H_2O)$,
- 8) $2\{Z\} \rightleftharpoons \{C = C\}$,

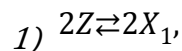
where Z – is an active place in a graphene oxide structure.

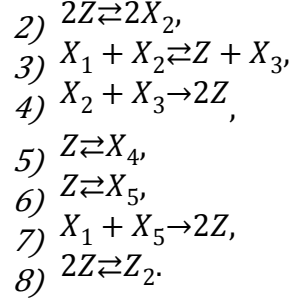
Generally, reactions (1), (5), (6) and (7) are characteristic for graphene oxide edges, including the edges of defects in the two-dimensional structure. The part of these places can be significant for real samples, and thus interaction between edges and volume can be significant too. We note that similar effects are typical for heterogeneous catalytic processes where surface processes often determine the state of the catalyst volume. Reactions (1), (6), (7) are the simplest catalytic trigger, i.e. the system with three steady states. Stage (5) leads to continuous oscillations. Accounting for the remaining stages causes decaying in time and unsteadiness.

Let us introduce the following notations:

$$ZO = X_1; ZH = X_2; ZOH = X_3; ZH_2O = X_4; ZH_2 = X_5; Z_2 = X_6.$$

The formal reaction scheme in this notation will be following:





For a specified set of steps, we can write the reaction rates:

- 1) $w_1 = k_1 z^2 - k_{-1} x_1^2$,
- 2) $w_2 = k_2 z^2 - k_{-2} x_2^2$,
- 3) $w_3 = k_3 x_1 x_2 - k_{-3} z x_3$,
- 4) $w_4 = k_4 x_2 x_3$,
- 5) $w_5 = k_5 z - k_{-5} x_4$,
- 6) $w_6 = k_6 z - k_{-6} x_5$,
- 7) $w_7 = k_7 x_1 x_5$,
- 8) $w_8 = k_8 z^2 - k_{-8} x_6$,

where:

$$k_1 = k_1 p_O,$$

$$k_2 = k_2 p_H,$$

$$k_5 = k_5 p_{H_2O},$$

$$k_6 = k_6 p_H.$$

and p_O, p_H, p_{H_2O} –are concentrations of $\{ZO\}$, $\{ZH\}$ and $\{ZH_2O\}$ respectively, which are assumed constant.

In this case, nonstationary kinetic model takes the form:

$$\begin{aligned}
 \frac{dx_1}{dt} &= 2w_1 - w_3 - w_7; \\
 \frac{dx_2}{dt} &= 2w_2 - w_3 - w_4; \\
 \frac{dx_3}{dt} &= w_3 - w_4; \\
 \frac{dx_4}{dt} &= w_5;
 \end{aligned} \tag{S1}$$

$$\frac{dx_5}{dt} = w_6 - w_7;$$

$$\frac{dx_6}{dt} = w_8$$

where $z = 1 - x_1 - x_2 - x_3 - x_4 - x_5 - 2x_6$ determined according to the law of conservation of mass.

The analysis of this system of nonlinear differential equations involved the following steps: numerical solution with the given initial conditions and parameters; analysis of the number and stability of steady states; bifurcation analysis, which highlighted the range of parameters leading to oscillations; study of dependence of self-oscillation characteristics (period and amplitude of oscillation) on the parameters.

Numerical result of the kinetic model with the parameter values listed below is shown on the Figure S5. Relative error was estimated equal to 5-10%.

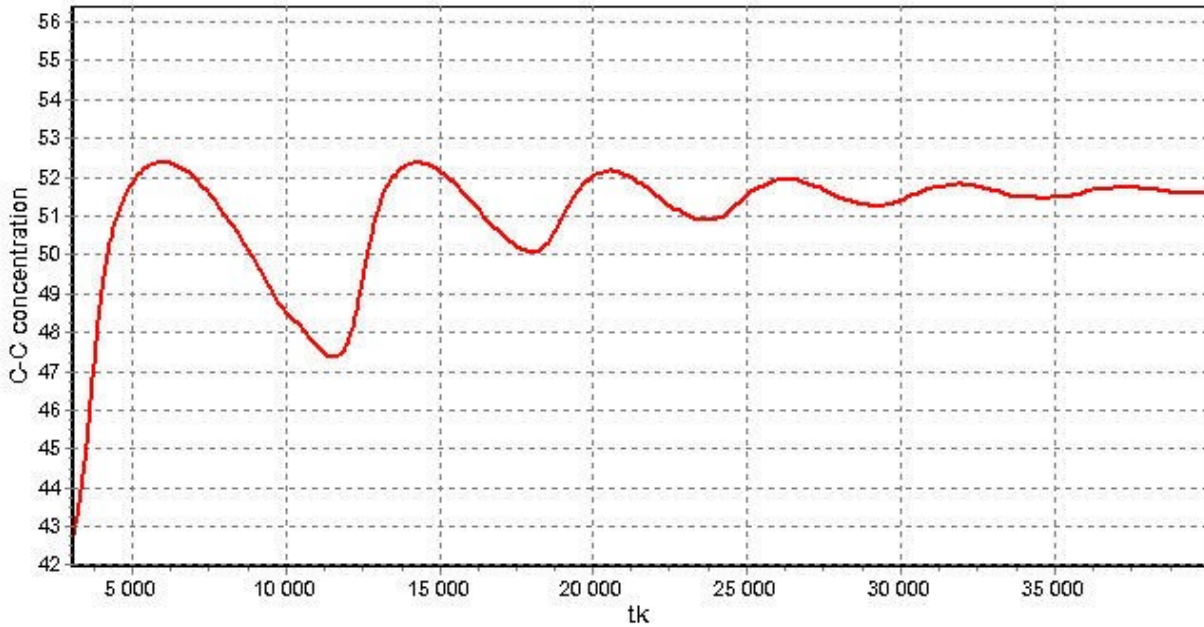


Figure S5. General behavior of time dependence of concentration “C-C” according to numerical solution of system of differential equations (S1) with the following parameters.

$$k_1$$

$$= 0.05, k_{-1} = 0.02, k_2 = 10^{-6}, k_{-2} = 2 \cdot 10^{-6}, k_3 = 0.2, k_{-3} = 2 \cdot 10^{-6},$$

$$\cdot 10^{-3}, k_{-5}$$

$$= 4.4 \cdot 10^{-4}, k_6 = 0.02, k_{-6} = 0.002, k_7 = 0.2, k_8 = 1.66 \cdot 10^{-6}, k_{-8} = 0.$$

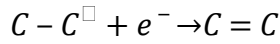
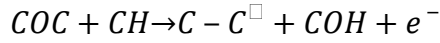
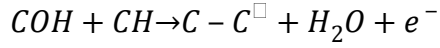
One of analytical solution of the system (S1) is:

$$C_1 - C_2 e^{-\frac{t}{k_1}} + C_3 e^{-\frac{t}{k_2}} \sin(k_3 t - k_4) \quad (\text{S2})$$

This equation was used for fitting of the experimental results shown in the main manuscript.

Diffusion model

This model is based on the chemical reactions:



To analyze diffusivity model we used the following differential equations:

$$\frac{dz}{dt} = I_1 x(t) - k_1 z(t) y(t) + k_2 p(t) y(t) \quad (\text{S4})$$

$$\frac{dy}{dt} = I_2 x(t) - k_1 z(t) y(t) - k_2 p(t) y(t) \quad (\text{S5})$$

$$\frac{dp}{dt} = I_3 x(t) - k_2 p(t) y(t) \quad (\text{S6})$$

$$\frac{dx}{dt} = k_1 z(t) y(t) - k_3 x(t) \quad (\text{S7})$$

where z- [C-OH], y- [C-H], p- [C-O-C], x- [C-C[•]], c- [C=C]. Adding (S4)- (S5)+2×(S6) have in steady state.

$$\frac{d(z - y + 2p)}{dt} = (I_1 - I_2 + 2I_3)x(t) = 0 \text{ . Which lead to } (I_1 - I_2 + 2I_3) = 0 \text{ or } x(t) = 0$$

Adding (S4)+ (S5)+2×(S7) we have for a steady state:

$$\frac{d(z + y + 2x)}{dt} = (I_1 + I_2 - 2k_3)x(t) = 0$$

Wherefrom $(I_1 + I_2 - 2k_3) = 0$ or $x(t) = 0$. Thus there are steady states where carbon radicals [C-C[•]] are absent and steady states with random carbon radical concentration occur only when

$(I_1 - I_2 + 2I_3) = 0$ and $(I_1 + I_2 - 2k_3) = 0$. Execution of the last equalities should have some reason, which we do not know.

Let us consider the case where there are no carbon radicals in a steady state $x(t) \equiv x_0 = 0$. Simultaneously, condition $z(t)y(t) = p(t)y(t) = 0$ should be satisfied, from which either 1) $y_0 = 0$, and z_0, p_0 - are arbitrary, or 2) $z_0, p_0 = 0$, and y_0 is arbitrary. Thus steady states lie in a ZP plane and the Y-axis, or in other words, in the steady state there are no [C-C*] and [C-H], or there are no [C-C*], [C-OH] and [C-O-C]. These conclusions seem reasonable for ideally reduced graphene oxide.

Let's analyze the stability of the obtained states.

1. The first case $y_0 = 0$, z_0, p_0 - are arbitrary.

Clear in advance that the two eigenvalues are equal to zero, because changing z_0, p_0 (the concentrations [C-OH], [C-O-C]) we remain in a steady state.

The equations for small variations:

$$z - z_0 = Ze^{\lambda t}, \quad y - y_0 = Ye^{\lambda t}, \quad p - p_0 = Pe^{\lambda t}, \quad x - x_0 \rightarrow Xe^{\lambda t}$$

$$\lambda z = I_1 x - (k_1 z_0 - k_2 p_0) y$$

$$\lambda y = I_2 x - (k_1 z_0 + k_2 p_0) y$$

$$\lambda p = I_3 x - k_2 p_0 y$$

$$\lambda x = k_1 z_0 y - k_3 x$$

$$\lambda x = -k_3 x + k_1 z_0 y$$

$$\lambda y = I_2 x - (k_1 z_0 + k_2 p_0) y$$

$$\lambda z = I_1 x - (k_1 z_0 - k_2 p_0) y$$

$$\lambda p = I_3 x - k_2 p_0 y$$

$$\lambda x = -k_3 x + k_1 z_0 y$$

$$\lambda y = I_2 x - (k_1 z_0 + k_2 p_0) y$$

$$(\lambda + k_3)(\lambda + k_1 z_0 + k_2 p_0) - k_1 z_0 I_2 = 0$$

$$\lambda^2 + (k_3 + k_1 z_0 + k_2 p_0)\lambda + k_3(k_1 z_0 + k_2 p_0) - k_1 z_0 I_2 = 0$$

$$\lambda_{\pm} = \frac{-(k_3 + k_1 z_0 + k_2 p_0) \pm \sqrt{(k_3 + k_1 z_0 + k_2 p_0)^2 - 4[k_3(k_1 z_0 + k_2 p_0) - k_1 z_0 I_2]}}{2}$$

$$\lambda_{\pm} = \frac{-(k_3 + k_1 z_0 + k_2 p_0) \pm \sqrt{(k_3 - k_1 z_0 - k_2 p_0)^2 + 4k_1 z_0 I_2}}{2}$$

Since $4k_1 z_0 I_2 > 0$ then $\lambda_+ > 0$ and all states are unstable.

2. Let us consider second case $z_0, p_0 = 0, y_0$ - is arbitrary.

$$\begin{aligned}
x - x_0 &\rightarrow xe^{\lambda t}, \quad y - y_0 \rightarrow ye^{\lambda t}, \quad p - p_0 \rightarrow pe^{\lambda t}, \quad z - z_0 \rightarrow ze^{\lambda t} \\
\lambda z &= I_1 x - k_1 z y_0 + k_2 p y_0 \\
\lambda y &= I_2 x - k_1 z y_0 - k_2 p y_0 \\
\lambda p &= I_3 x - k_2 p y_0 \\
\lambda x &= k_1 z y_0 - k_3 x
\end{aligned} \tag{S8}$$

Wherein we know in advance that due to degeneracy of the ground state, one of the eigenvalues is equal to zero (arbitrary shift along the Y-axis leaves the system in a steady state). From the last two equations we find

$$x = \frac{k_1 z y_0}{\lambda + k_3}, \quad p = \frac{I_3 x}{\lambda + k_2} = \frac{I_3 k_1 z y_0}{(\lambda + k_2)(\lambda + k_3)} \tag{S9}$$

Thus one system of two equations is remained

$$\begin{aligned}
\lambda z &= I_1 x - k_1 z y_0 + k_2 p y_0 = I_1 \frac{k_1 z y_0}{\lambda + k_3} - k_1 z y_0 + \frac{I_3 k_1 k_2 y_0^2 z}{(\lambda + k_2)(\lambda + k_3)} \\
\lambda y &= I_2 x - k_1 z y_0 - k_2 p y_0
\end{aligned} \tag{S10}$$

The eigenvalues are determined from the first equation (S4). After that let's express all concentrations in terms of z using (S5) and (S9):

$$\begin{aligned}
\lambda(\lambda + k_2)(\lambda + k_3) &= I_1 k_1 y_0 (\lambda + k_2) - k_1 y_0 (\lambda + k_2)(\lambda + k_3) + I_3 k_1 k_2 y_0^2 \\
\lambda^3 + (k_2 + k_3 - k_1 y_0)\lambda^2 + (k_2 k_3 - I_1 k_1 y_0 + k_1 y_0 (k_2 + k_3))\lambda - (I_1 k_1 k_2 y_0 + k_1 y_0 k_2 k_3 - I_3 k_1 k_2 y_0^2) &= 0 \\
\lambda^3 + (k_2 + k_3 - k_1 y_0)\lambda^2 + (k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1))\lambda - (I_1 + k_3 - I_3 y_0)k_1 k_2 y_0 &= 0
\end{aligned} \tag{S11}$$

If $(k_2 + k_3 - k_1 y_0) < 0$, then sum of all eigenvectors are positive $\lambda_1 + \lambda_2 + \lambda_3 > 0$. If $(I_1 + k_3 - I_3 y_0) > 0$ then $\lambda_1 \lambda_2 \lambda_3 > 0$. In the both cases, one of the eigenvectors more than zero and state is unstable.

For getting steady state, all roots of polynomial:

$$P(\lambda) = \lambda^3 + (k_2 + k_3 - k_1 y_0)\lambda^2 + (k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1))\lambda - (I_1 + k_3 - I_3 y_0)k_1 k_2 y_0$$

should have negative real part. For this purpose it is necessary and sufficient that the roots of the auxiliary equation $P(\lambda)' = 3\lambda^2 + 2(k_2 + k_3 - k_1 y_0)\lambda + (k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1)) = 0$ should have negative real part and $P(0) > 0$.

$$1.1. \quad P(0) > 0 \text{ if } (I_1 + k_3 - I_3 y_0) < 0, \quad y_0 > \frac{I_1 + k_3}{I_3}$$

1.2. The roots of the auxiliary equation

$$\lambda^2 + \frac{2}{3}(k_2 + k_3 - k_1 y_0)\lambda + \frac{1}{3}(k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1)) = 0$$

$$\operatorname{Re}\left[-\frac{1}{3}(k_2 + k_3 - k_1 y_0) \pm \sqrt{\left[\frac{1}{3}(k_2 + k_3 - k_1 y_0)\right]^2 - \frac{1}{3}(k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1))}\right] < 0$$

$$k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1) > 0 \quad y_0 > \frac{k_2 k_3}{k_1 (k_2 + k_3 - I_1)}$$

Thus if $y_0 > \frac{I_1 + k_3}{I_3}$; $y_0 > \frac{k_2 k_3}{k_1 (k_2 + k_3 - I_1)}$ then states are steady.

In addition, if $[(k_2 + k_3 - k_1 y_0)]^2 - 3(k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1)) < 0$ then oscillations should appear during relaxation and:

$$\begin{aligned} & [(k_2 + k_3 - (k_1 y_0))]^2 - 3(k_2 k_3 + k_1 y_0 (k_2 + k_3 - I_1)) = \\ & (k_1 y_0)^2 - [5(k_2 + k_3) - 3I_1](k_1 y_0) + [(k_2 + k_3)^2 - 3k_2 k_3] < 0 \\ & (k_1 y_0)_{\pm} = \frac{[5(k_2 + k_3) - 3I_1] \pm \sqrt{[5(k_2 + k_3) - 3I_1]^2 - 4[(k_2 - k_3)^2 + k_2 k_3]}}{2} \end{aligned}$$

In other words, at small deviations, the relaxation oscillations aspires to states:

$$y_0 > \frac{I_1 + k_3}{I_3}; \quad y_0 > \frac{k_2 k_3}{k_1 (k_2 + k_3 - I_1)}; \quad (k_1 y_0)_+ > (k_1 y_0) > (k_1 y_0)_-$$

If $[5(k_2 + k_3) - 3I_1]^2 - 4[(k_2 - k_3)^2 + k_2 k_3] < 0$, then there are no stationary points of oscillatory relaxation. If the auxiliary equation has no real roots, then the basic equation has only one real root. However, it is not sufficient, as one real root exist even when the auxiliary equation has real roots.

Thus, oscillation relaxation possible for certain values of the parameters for small deviations from the steady state and very likely for large deviations.

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