Chemical Instabilities during Oxidation of 1,4-Naphthalenediol in a Homogeneous Medium: II. Thermodynamic Analysis and Mathematical Modeling

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Received October 26, 2006

Abstract—A possible mechanism of 1,4-naphthalenediol oxidation in the oscillatory regime has been considered, and a mathematical model describing the kinetics has been developed. Based on a thermodynamic Lyapunov function, it has been shown that the source of chemical instabilities is in the existence of autocatalytic steps and dynamic feedbacks. Qualitative analysis and numerical solution of the set of differential equations that model the reaction kinetics have been performed. The character of the stationary state and the possibility of bifurcations have been determined. The mathematical model satisfactorily describes the processes occurring in the system.

DOI: 10.3103/S0027131407040128

1. THERMODYNAMIC ANALYSIS OF 1,4-NAPHTHALENEDIOL OXIDATION IN THE OSCILLATORY REGIME

One of the important problems in the study of oscillatory chemical reactions is to reveal the possibility and origin of the emergence of critical phenomena on the basis of the principles of nonequilibrium nonlinear thermodynamics. To determine the thermodynamic stability of a system under highly nonequilibrium conditions, the derivative of the second variation of entropy is estimated, which is a Lyapunov function for the stationary state [1]. Thus, if $(\partial/\partial t)\rho\delta^2 S \geq 0$, the stationary state far from equilibrium is stable; if $(\partial/\partial t)\rho\delta^2 S < 0$, it is unstable and the emergence of dissipative structures is possible (ρ is the average density).

To estimate the stability of a system, the equation for the derivative of the second variation of entropy is used in the following form [1]:

$$\int_V (\partial/\partial t)\rho\delta^2 S dV = \int_{F_s} \delta(\mu_k/T)\delta x_k v^n dF_s$$

$$+ \int_{F_s} -\delta T^{-1}\delta q_1^n dF_s + \int_V \delta w \delta(A_w/T)dV$$

$$= \int_{F_s} \delta(\mu_k/T)\delta x_k v^n dF_s + \int_V \delta w \delta(A_w/T)dV$$

$$+ K_T F_s(\delta T)^2/T^2 + \rho C_T v_q(\delta T)^2/T, \quad (1)$$

where A_w is the chemical reaction affinity, w is the reaction rate, V is the working volume of the reactor, F_s is the surface of the reactor, q_1^n is the heat flux through the surface, μ_k is the chemical potential of the kth component, v is the solution flow rate, T is the temperature, C_T is the heat capacity, and K_T is the heat transfer coefficient.

For processes that occur in a static reactor, the term $\int_{F_s} \delta(\mu_k/T)\delta x_k v^n dF_s$, which characterizes mass exchange with the environment, can be taken as zero ($\delta x_k = 0$), and the equation for the derivative of the second variation of entropy is rearranged to the form:
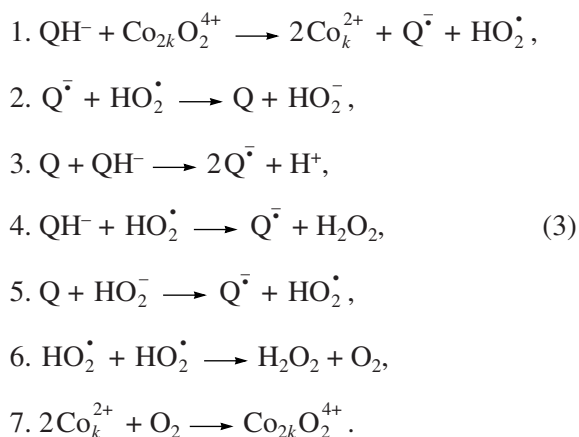
$$\int_V \delta w \delta(A_w/T)dV + K_T F_s(\delta T)^2/T^2 + \rho C_T v_q(\delta T)^2/T. \quad (2)$$

As follows from expression (2), to estimate $(\partial/\partial t)\rho\delta^2 S dV$, the product $\delta w \delta(A_w/T)dV$ should be calculated for definite kinetic schemes of the elementary steps of a complex reaction.

To verify the mechanism of 1,4-naphthalenediol (QH_2) oxidation in the oscillatory regime, the following facts [2–4] were taken into account: (i) the process was carried out at pH 7.77–8.14, at which 1,4-naphthalenediol is mainly in the QH^- form [2]; (ii) the oxidant was molecular oxygen reversibly bound to heteroligand cobalt(II) complexes with DMG and Py [3]; (iii)

according to [4], the process involved the formation of $Q^{\cdot -}$, $HO_2^{\cdot}$, and HO_2^- species.

From these considerations, the scheme of the processes occurring during oxidation can be represented as

$$1.\ QH^- + Co_{2k}O_2^{4+} \longrightarrow 2Co_k^{2+} + Q^{\cdot -} + HO_2^{\cdot},$$

$$2.\ Q^{\cdot -} + HO_2^{\cdot} \longrightarrow Q + HO_2^-,$$

$$3.\ Q + QH^- \longrightarrow 2Q^{\cdot -} + H^+,$$

$$4.\ QH^- + HO_2^{\cdot} \longrightarrow Q^{\cdot -} + H_2O_2, \qquad (3)$$

$$5.\ Q + HO_2^- \longrightarrow Q^{\cdot -} + HO_2^{\cdot},$$

$$6.\ HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2 + O_2,$$

$$7.\ 2Co_k^{2+} + O_2 \longrightarrow Co_{2k}O_2^{4+}.$$

Here, QH^-, $Q^{\cdot -}$, and Q are different species forming in the course of 1,4-naphthalenediol transformation; $Co_{2k}O_2^{4+}$ and Co_k^{2+} are the oxygenated and unoxygenated forms of cobalt(II) complexes. Let us introduce the following notations: $[QH^-]_{initial} = a$, $[Co_{2k}O_2^{4+}] = b$, $[Q^{\cdot -}] = x$, $[HO_2^{\cdot}] = y$, $[Q] = z$, and $[QH^-] = a - x - z = h$. Then, the derivative of the thermodynamic Lyapunov function (excess entropy production) for the above kinetic scheme has the following explicit form (the procedure of calculation of δw and $\delta (A_w/T)$ was reported in [5]):

$$\delta w_i \delta (A_{wi}/T) dV = V\left\{ [(\delta x/x)^2 R w_2 \right.$$

$$+ (\delta y/y)^2 R(w_2 + w_4 + 4w_6) + (\delta z/z)^2 R(w_3 + w_5)$$

$$+ (\delta h/h)^2 R(w_1 + w_3 + w_5)$$

$$+ (\delta x/x)(\delta y/y) R(2w_2 - w_4)$$

$$+ (\delta x/x)(\delta z/z) R(-w_2 - 2w_3 - w_5)$$

$$+ (\delta x/x)(\delta h/h) R(-w_1 - 2w_3 - w_4)$$

$$+ (\delta y/y)(\delta z/z) R(-w_2 - w_5)$$

$$+ (\delta y/y)(\delta h/h) R(-w_1 + 2w_4) + (\delta z/z)(\delta h/h) 2R w_3]$$

$$+ (\delta T/T^2)(\delta x/x)[-w_1 E_1 - w_2(Q_2 - E_2) - 2w_3 E_3$$

$$- w_4 E_4 - w_5 E_5)] + (\delta T/T^2)(\delta y/y)[-w_1 E_1$$

$$- w_2(Q_2 - E_2) - w_4(Q_4 - E_4) - w_5 E_5 - w_6(Q_6 + E_6)]$$

$$+ (\delta T/T^2)(\delta z/z)[-w_2 E_2 - w_3(Q_3 - E_3)$$

$$- w_5(Q_5 - E_5)] + (\delta T/T^2)(\delta h/h)[-w_1(Q_1 - E_1)$$

$$- w_3(Q_3 - E_3) - w_4(Q_4 - E_4)]$$

$$+ \left[(\delta T^2/T)(-1/RT^2) \sum_{i=1}^{7} w_i E_i Q_i \right.$$

$$\left. \left. + K_T F_s/V + \rho v_q C_T/V \right] \right\}. \qquad (4)$$

Analysis of Eq. (4) shows that the terms corresponding to the forward reactions—$(\delta x/x)^2 R w_2 + (\delta y/y)^2 R(w_2 + w_4 + 4w_6) + (\delta z/z)^2 R(w_3 + w_5) + (\delta h/h)^2 R(w_1 + w_3 + w_5)$—are positive, which favors the stability of the system. In such systems, thermal instabilities can emerge when the term $(-1/RT^2) \sum_{i=1}^{7} w_i E_i Q_i$, which characterizes the heat of the chemical reaction, becomes larger than the term $K_T F_s/V$, related to heat removal, i.e., at rather high heats of reaction and insufficient heat removal.

The kinetic schemes show that autocatalytic formation of one of the components, $Q^{\cdot -}$, is ensured by steps (2) and (3). In this case, the terms

$$[(\delta x/x)(\delta z/z) R(w_2 + 2w_3)$$

$$+ 2(\delta x/x)(\delta h/h) R w_3 + (\delta y/y)(\delta z/z) R w_2]$$

in Eq. (4) are negative.

If the contribution of these terms predominates, the process can become unstable and critical phenomena can emerge.

It follows from kinetic schemes (3) that the feedback is due to the formation of $Q^{\cdot -}$ through the reaction of QH_2 with $HO_2^{\cdot}$ (steps 1 and 4). In this case, the terms with negative sign

$$-R[(\delta x/x)(\delta y/y) w_4 + (\delta x/x)(\delta h/h)(w_1 + w_4)$$

$$+ (\delta y/y)(\delta h/h) w_1]$$

appear in the expression for the derivative of the second variation of entropy. If the contribution of these terms predominates, the transition of the system to instability is probable.

In the derivative of the thermodynamic Lyapunov function, the terms responsible for the onset of thermokinetic oscillations and related to autocatalysis have the form

$$-\{[(\delta T/T^2)(\delta x/x)[w_2(Q_2 - E_2) + 2w_3 E_3]$$

$$+ (\delta T/T^2)(\delta y/y)[w_2(Q_2 - E_2)]$$

$$+ (\delta T/T^2)(\delta z/z)[w_2 E_2 + w_3(Q_3 - E_3)]$$

$$+ (\delta T/T^2)(\delta h/h)[w_3(Q_3 - E_3)]\}.$$

If an increase in temperature promotes steps 2 and 3, the $Q^{\cdot-}$ radical anion can accumulate in the system ($\delta T > 0 \longrightarrow \delta x > 0$) and the above terms thereby can become more negative, so that the system will become more destabilized. The existence of feedbacks can also lead to instability of the system. The terms

$$-\{(\delta T/T^2)(\delta x/x)[w_1 E_1 + w_4 E_4]$$

$$+ (\delta T/T^2)(\delta y/y)[w_1 E_1 + w_4(Q_4 - E_4)]$$

$$+ (\delta T/T^2)(\delta h/h)[w_1(Q_1 - E_1) + w_4(Q_4 - E_4)]\}$$

are related to the feedbacks. If these terms predominate, critical phenomena will be possible.

Thus, our thermodynamic analysis based on estimation of the derivative of the second variation as a Lyapunov function allows us to conclude that the onset of chemical oscillations in the system under consideration is due to the existence of autocatalytic steps and dynamic and thermokinetic feedbacks. At the same time, it should be emphasized that the above kinetic scheme can be considered as an alternative to the emergence of the oscillatory regime in the homogeneous system under consideration.

2. DEVELOPMENT AND ANALYSIS OF THE MATHEMATICAL MODEL

Mathematical models are sets of ordinary nonlinear differential equations deduced based on the consideration of the mechanisms of chemical processes. In this work, after some simplifications (taking into account the dimension of the chemical system and the constancy of the pH and oxygen solubility in water, assuming some steps to be quasi-stationary), the mathematical model consistent with the kinetic schemes of 1,4-naphthalenediol oxidation in the presence of oxygenated cobalt(II) complexes is represented by the set of three nonlinear differential equations

$$dC_X/dt' = k_1(C_A - C_X - C_Z)C_B - k_2 C_X C_Y$$

$$+ 2k_3(C_A - C_X - C_Z)C_Z + k_4(C_Y - C_X - C_Z)C_Y$$

$$+ k_5 C_Z;$$

$$dC_Y/dt' = k_1(C_A - C_X - C_Z)C_B - k_2 C_X C_Y \tag{5}$$

$$- k_4(C_A - C_X - C_Z)C_Y + k_5 C_Z - k_6 C_Y^2;$$

$$dC_Z/dt' = k_2 C_X C_Y - k_3(C_A - C_X - C_Z)C_Z - k_5 C_Z,$$

where $C_X = [Q^{\cdot-}]$, $C_Y = [HO_2^{\cdot}]$, $C_Z = [Q]$, $C_A = C_{R(\text{initial})}$, $C_B = C_{\text{cat(initial)}}$, $C_{R(\text{initial})} = [QH_2] + [Q^{\cdot-}] + [Q]$, and t' is time.

Qualitative analysis of this mathematical model and its numerical solution were performed using a common procedure for determining specific features of process dynamics.

2.1. Qualitative Analysis of the Mathematical Model

To solve this problem, the set was first reduced to the following dimensionless form [6]:

$$\varepsilon dx/dt = (\mu a - \rho^{-1}x - \mu\xi z)b - xy$$

$$+ 2(\mu\xi\rho a - \xi x - \mu\xi^2\rho z)z$$

$$+ (\mu\rho\varphi a - \varphi x - \mu\xi\rho\varphi z)y + z, \tag{6}$$

$$\varepsilon' dy/dt = (\mu a - \rho^{-1}x - \mu\xi z)b - xy$$

$$- (\mu\rho\varphi a - \varphi x - \mu\xi\rho\varphi z)y + z - \sigma y^2,$$

$$dz/dt = xy - 2(\mu\xi\rho a - \xi x - \mu\xi^2\rho z)z - z,$$

where $\omega = k_3/k_2$; $\eta = k_2/k_3$; $\varepsilon = k_5/k_2$, $\delta = k_5$, $\mu = k_1/k_2$, $\rho = k_3/k_1$, $\xi = k_2/k_5$, $\varphi = k_4/k_2$, $\sigma = k_3^2 k_6/k_2^3$, and $\varepsilon' = k_3 k_5/k_2^2$.

For qualitative analysis, the stationary state should be determined. To do this, the left-hand sides of the equations are equated to zero and the set of algebraic equations (7) is solved:

$$(\mu\alpha - \rho^{-1}x - \mu\xi z)b - xy + 2(\mu\xi\rho\alpha - \xi x - \mu\xi^2\rho z)z$$

$$+ (\mu\rho\varphi a - \varphi x - \mu\xi\rho\varphi z)y + z = 0,$$

$$(\mu\alpha - \rho^{-1}x - \mu\xi z)b - xy - (\mu\rho\varphi\alpha - \varphi x - \mu\xi\rho\varphi z)y \tag{7}$$

$$+ z - \sigma y^2 = 0,$$

$$xy - 2(\mu\xi\rho\alpha - \xi x - \mu\xi^2\rho z)z - z = 0.$$

It can be shown that the coordinates of the stationary (singular) point correspond to
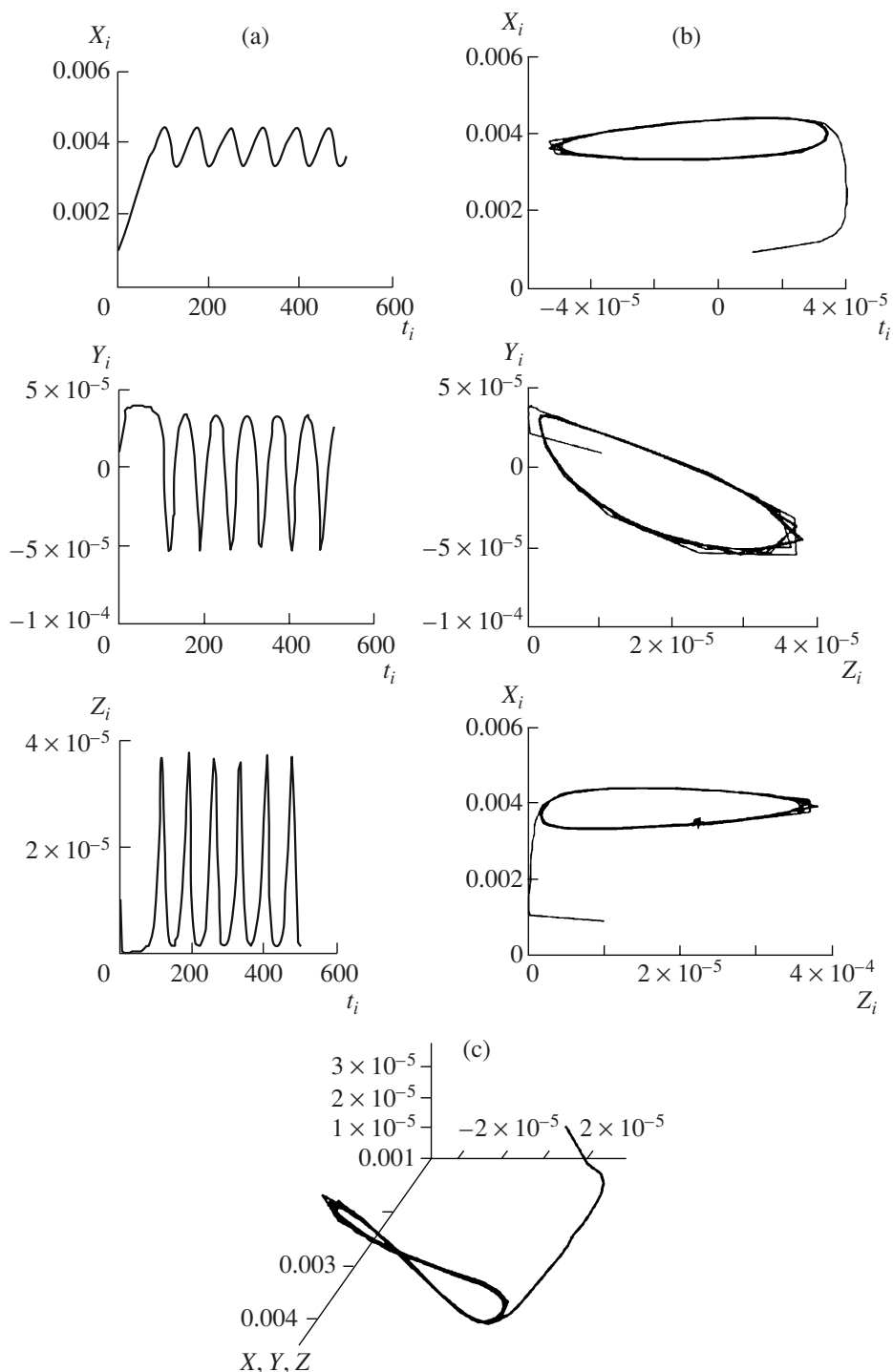
$$\bar{x} = \alpha\mu\rho; \quad \bar{y} = 0; \quad \bar{z} = 0.$$

The Routh–Hurwitz matrix, which is used for examining the stability of this stationary state, is

$$\begin{vmatrix} -\rho^{-1}b - \lambda & -\alpha\mu\rho & -\mu\xi b + 1 \\ -\rho^{-1}b & -\alpha\mu\rho - \lambda & -\mu\xi b + 1 \\ 0 & \alpha\mu\rho & -1 - \lambda \end{vmatrix} = 0. \tag{8}$$

Hence, we obtain that the coefficients of the characteristic polynomial

$$\lambda^3 + A_1\lambda + A_2\lambda + A_3 = 0 \tag{9}$$

Fig. 1. (a) Concentrations of species X_i, Y_i, and Z_i as a function of time. (b and c) Phase portraits of systems in coordinates (b) X_i–Y_i, Y_i–Z_i, X_i–Z_i and (c) X_i–Y_i–Z_i ($a = 3.0 \times 10^{-3}$, $b = 1.0 \times 10^{-4}$).

are as follows:

$$A_1 = (\rho^{-1}b + \alpha\mu\rho + 1);$$

$$A_2 = (\rho^{-1}b + ab\mu^2\xi\rho); \quad A_3 = 0. \tag{10}$$

Then, the roots of characteristic equation (10) correspond to $\lambda_1 = 0$, $\lambda_2 \neq 0$, and $\lambda_3 \neq 0$.

In the case when one of the roots is zero, qualitative structures change in the vicinity of the stationary state when passing through the boundary of the Routh–Hurwitz region, and a double singularity is realized [7]. Analysis of the expression $\Delta^* = -A_1^2 A_2^2 + 4A_3^3$ using the procedure considered in [7] shows that, at $\Delta^* < 0$
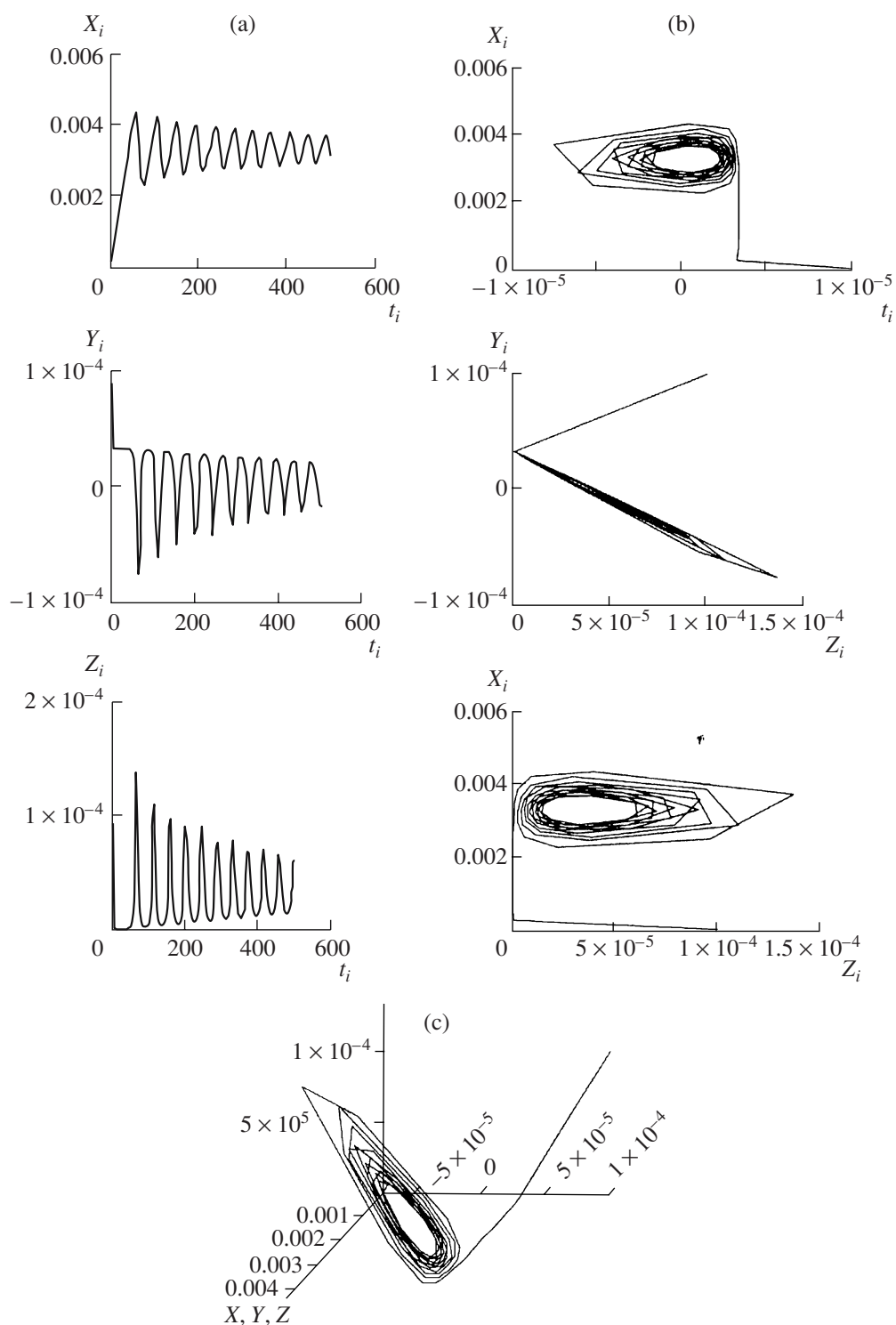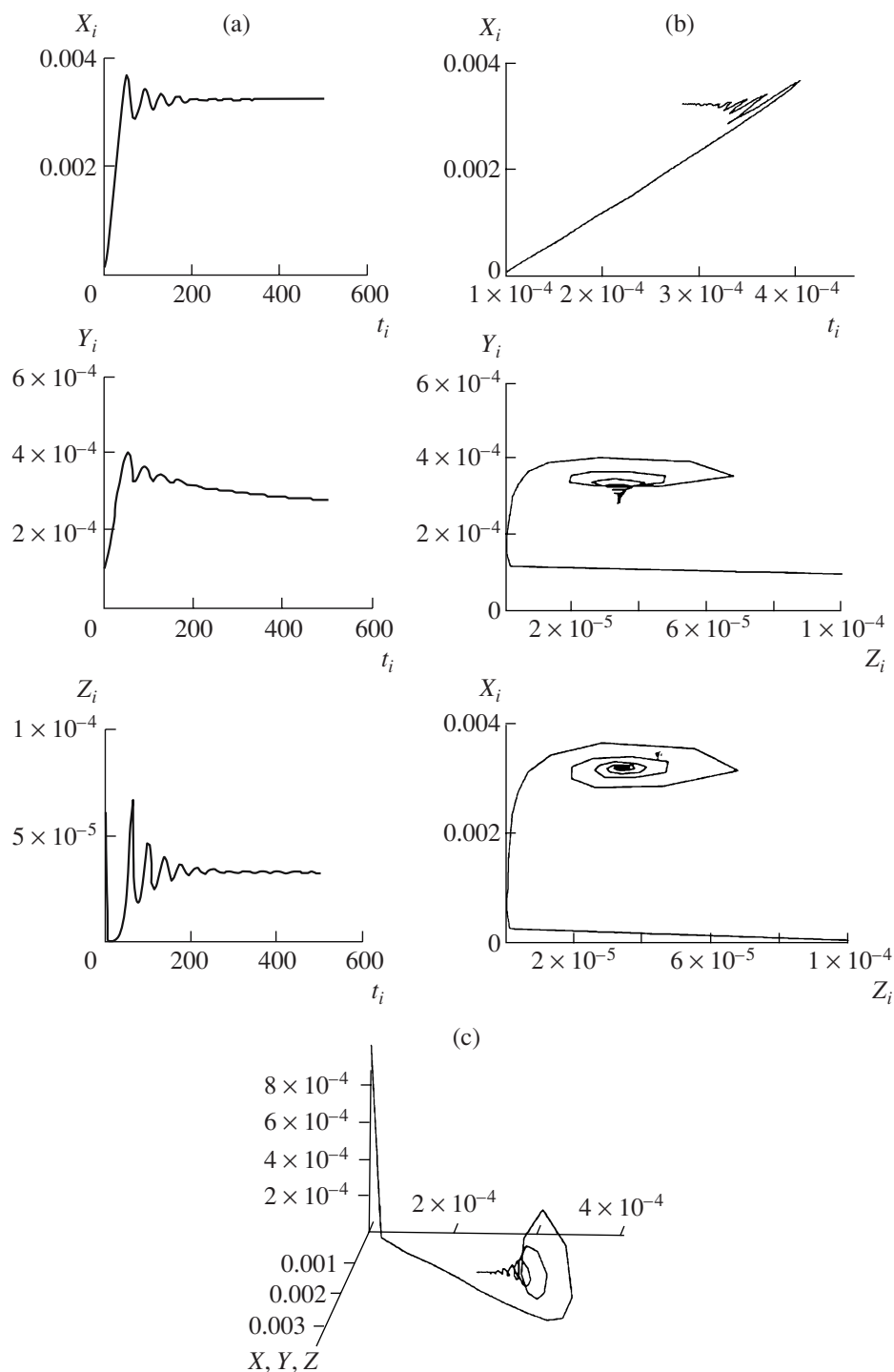
Fig. 2. (a) Concentrations of species X_i, Y_i, and Z_i as a function of time. (b and c) Phase portraits of systems in coordinates (b) X_i–Y_i, Y_i–Z_i, X_i–Z_i and (c) X_i–Y_i–Z_i ($a = 1.0 \times 10^{-2}$, $b = 1.0 \times 10^{-4}$).

(or $\left| A_1^2 A_2^2 \right| > \left| 4 A_3^3 \right|$), the above stationary state can become unstable, the singularity being of the saddle–focus type. From this stationary state, bifurcation to a limit cycle is possible; i.e., the emergence of an oscillatory regime is possible.

2.2. Numerical Integration of the Mathematical Model

A major task in numerical solution of a mathematical model is finding the parameter domain in which the emergence of chemical instabilities is possible [8]. For solving the sets of ordinary differential equations, we

Fig. 3. (a) Concentrations of species X_i, Y_i, and Z_i as a function of time. (b and c) Phase portraits of systems in coordinates (b) X_i–Y_i, Y_i–Z_i, X_i–Z_i and (c) X_i–Y_i–Z_i ($a = 3.0 \times 10^{-3}$, $b = 1.0 \times 10^{-3}$).

used the Mathcad program with the Rkadapt subroutine, which is internally adapted to the integration step [9]. Our primary concern was determining the reagent and catalyst concentration limits for the emergence of oscillations. Figure 1 shows (a) the calculated trajectories of the dynamic system and (b and c) its phase portraits for the case when $a = 3.0 \times 10^{-3}$ and $b = 1.0 \times 10^{-4}$

(the number of points was taken to be 600, and the step corresponds to 1). The results of the numerical experiment show that, under these conditions, undamped oscillations occur and the phase portraits have the form of a limit cycle (conditions are listed in the figure captions; $X_i = [Q^{\bullet}]$, $Y_i = [HO_2^{\bullet}]$, and $Z_i = [Q]$).

The data in Figs. 2 and 3 illustrate the character of the evolution of the dynamics of the processes that occur in the system as a function of the governing parameters, the concentrations of the reagent (a) and catalyst (b). These data indicate that, at a and b values other than the aforementioned ones, damped oscillations can emerge.

Thus, the results of the numerical experiments allow us to conclude that the model satisfactorily describes the processes during the oxidation of 1,4-naphthalenediol in the oscillatory regime. At the same time, it is worth noting that, for a more adequate quantitative description, the mathematical model should be more complex and the numerical values of rate constants of definite steps should be taken into account.

ACKNOWLEDGMENTS

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