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Chemical Instabilities in Oxidation of 1,4-Naphthalenediol in Homogeneous Medium: I. The Deterministic Character of 1,4-Naphthodiol Oxidation and Its Quantitative Parameters

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Abstract—The chemical oscillatory processes that occur upon oxidation of 1,4-naphthalenediol in the presence of oxygenated cobalt(II) complexes in a homogeneous medium have been studied. The limits of the reagent and catalyst concentrations, pH, and temperature at which chemical oscillations are generated have been determined. The types of dynamics of the occurring processes and the dynamic parameters have been determined based on discrete Fourier transform, reconstruction of dynamics from time series of data, and calculations of the Lyapunov characteristic exponents and the Kolmogorov–Sinai entropy.

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Generation of self-oscillations and dynamic chaos in different systems has attracted the attention of researchers [1, 2]. Of special interest are nonlinear processes revealed through the study of a new class of chemical oscillatory reactions proceeding in simple biosubstrate/oxygenated transition metal complex systems. They show a number of examples of dynamic self-organization [3, 4].

In the present paper, we report the quantitative estimates of the dynamic characteristics of chemical oscillations that upon oxidation of 1,4-naphthalenediol (R) in the presence of oxygenated cobalt(II) complexes with dimethylglyoxime (DMG) and pyridine (Py).

RESULTS AND DISCUSSION

The study was based on the methodological approach used previously for studying oscillatory redox transformations of different biosubstrates; experimental details were described in [4].

Figure 1 show characteristic curves of the change in the platinum electrode potential versus time for $C_R = 3.0 \times 10^{-3}$ mol/L, $C_{\text{cat}} = 1.0 \times 10^{-4}$ mol/L, $T = 50°\text{C}$, and pH 7.96. These curves indicate that chemical oscillations are generated in the course of oxidation of 1,4-naphthalenediol in the presence of oxygenated cobalt(II) complexes with DMG and Py. These results allow us to state that a new homogeneous system in which concentration oscillations are generated has been found. Some characteristics of oscillations observed under different conditions (reagent and catalyst concentrations, temperature, and pH) are summarized in Table 1.

We found experimentally that concentration oscillations in this system are observed at the following values of parameters: $C_R = (1.5–3.5) \times 10^{-3}$ mol/L, $C_{\text{cat}} = (0.75–1.25) \times 10^{-4}$ mol/L, $T = 45–60°\text{C}$, and pH 7.7–8.2.

Analysis of Time Series

As a result of the experimental study of the oxidation of 1,4-naphthalenediol in the presence of oxygenated cobalt(II) complexes with DMG and Py, we obtained time series of data. The basic problem in analysis of such experimental results is to determine parameters that can identify the dynamics of the system to be studied. To do this, we applied a complex approach involving the use of discrete Fourier transform (DFT), reconstruction of the dynamics of time series with construction of phase portraits and determination of the dimensions of the phase space and attractor, and calculations of the Lyapunov exponents and the Kolmogorov–Sinai entropy.

Analysis of Fourier Transform of a Time Series

Time series were processed by the numerical DFT method using a routine computation program. The power spectrum corresponding to the case in Fig. 1 is shown in Fig. 2.

Fourier analysis of the time series obtained in this work shows that in none of the experiments did we reveal frequencies and, hence, chaotic oscillations

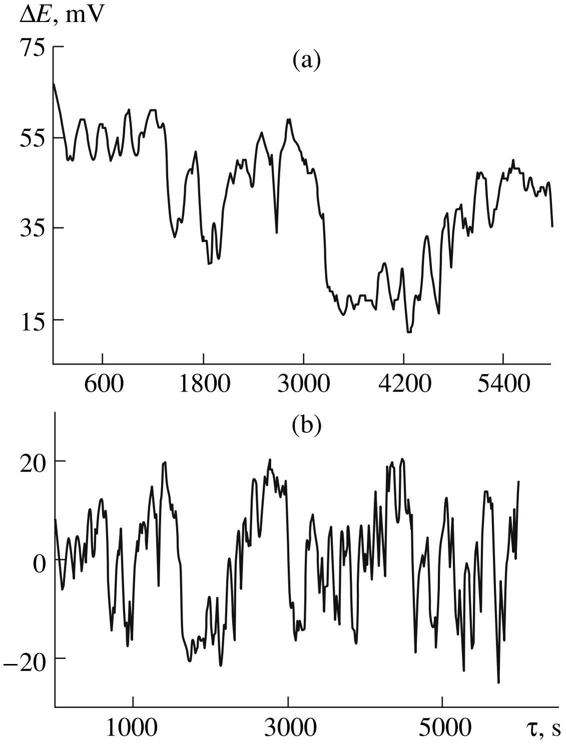

Fig. 1. Relative potential as a function of time: (*a*) the initial curve, and (*b*) after the removal of the trend.

occurred. In addition, the analysis allows us to draw the tentative conclusion that the observed chemical oscillations are a result of redox processes in the system, which points to the deterministic character of fluctuation phenomena.

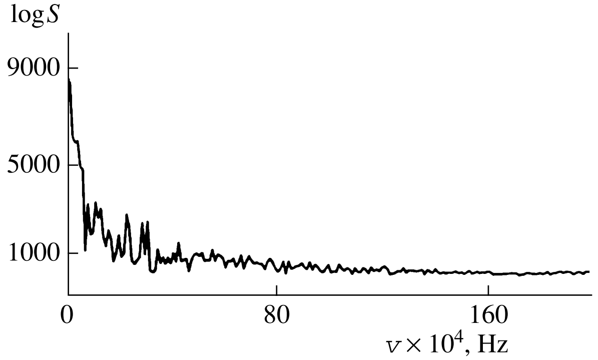

Fig. 2. Fourier spectrum of the time series.

Fourier transform does not allow one to distinguish between dynamic chaos and a random process. This limitation compels us to use other methods that provide more specific information on the dynamics of the processes in the system.

Construction of Phase Portraits

For description of the dynamics of a process in which chemical instabilities appear, definite information can be obtained based on the form of its phase space [5]. To construct phase portraits, we used a method in which $\Delta E_{\tau + 2\Delta\tau}$, $\Delta E_{\tau + \Delta\tau}$, ΔE_{τ} are used as coordinates (ΔE_{τ} is the value of the function at the instant τ, and $\Delta E_{\tau + \Delta\tau}$ and $\Delta E_{\tau + 2\Delta\tau}$ are the values of the same function at the instant $\tau + \Delta\tau$ and $\tau + 2\Delta\tau$, respectively).

Table 1. Characteristics of the oxidation of 1,4-naphthalenediol in the oscillatory mode

$C_{cat} = 1.0 \times 10^{-4}$ mol/L; $T = 50$°C; pH 7.96					
$C_R \times 10^3$, mol/L	1.5	2.0	2.5	3.0	3.5
Induction period, min	33	27	21	18	12
Amplitude, mV	12 ± 2	21 ± 3	32 ± 3	43 ± 4	10 ± 2
$C_R = 3.0 \times 10^{-3}$ mol/L; $T = 50$°C; pH 7.96					
$C_{cat} \times 10^{-4}$, mol/L	0.75	1.00		1.25	
Induction period, min	28	18		45	
Amplitude, mV	10 ± 2	43 ± 4		18 ± 2	
$C_R = 3.0 \times 10^{-3}$ mol/L; $C_{cat} = 1.0 \times 10^{-4}$ mol/L; $T = 50$°C					
pH	7.77	7.87	7.96	8.05	8.14
Induction period, min	9	32	18	22	25
Amplitude, mV	22 ± 2	30 ± 3	43 ± 4	25 ± 2	20 ± 2
$C_R = 3.0 \times 10^{-3}$ mol/L; $C_{cat} = 1.0 \times 10^{-4}$ mol/L; pH 7.96					
T, °C	45	50		55	
Induction period, min	14	18		50	
Amplitude, mV	23 ± 2	43 ± 4		10 ± 2	

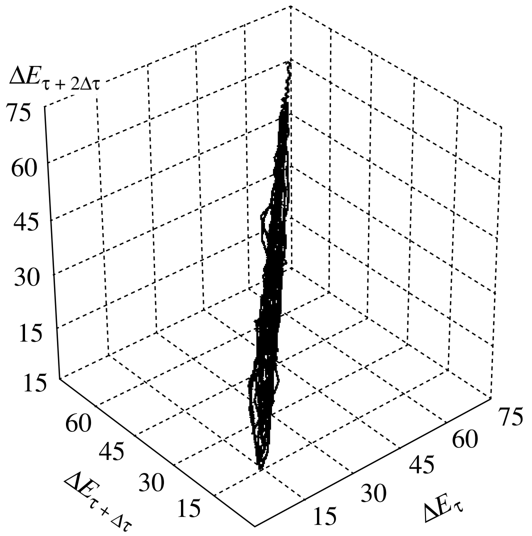

Fig. 3. Phase portrait in coordinates $\Delta E(t)$–$\Delta E(t + \Delta t)$–$\Delta E(t + 2\Delta t)$.

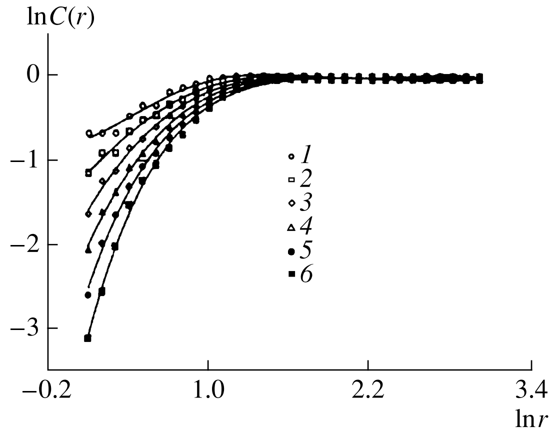

Fig. 4. $\ln C(r)$ vs. $\ln r$ at n = (*1*) 1, (*2*) 3, (*3*) 4, (*4*) 5, (*5*) 6, and (*6*) 7.

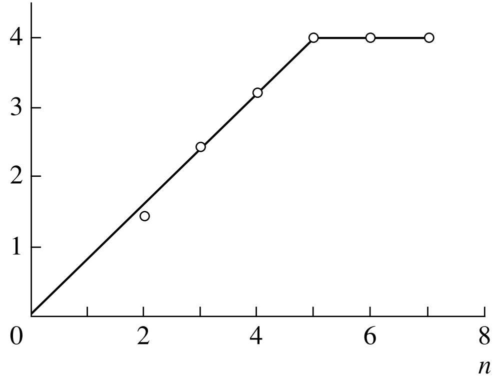

Fig. 5. Plot of d vs. n.

The three-dimensional phase portraits obtained based on the experimental time series at $\Delta\tau = 6$ s (see Fig. 1) are shown in Fig. 3, which demonstrates that all families of phase trajectories converge to a definite subset of points of the phase space, the attractor. This fact is evidence of a complicated character of the occurring processes and supports the deterministic character of their dynamics under the studied conditions.

Determination of the Dimensions of the Phase Space and Attractor

The dimensions of the phase space and attractor were estimated by means of the correlation integral presented in the form [6]

$$C(r) = \lim_{N \to \infty} (1/N^2) \sum_{i,\, j = 1,\, i \neq j}^{N} \theta(r - |x_i - x_j|),$$

where θ is the Heaviside function ($\theta(x) = 0$ at $x < 0$ and $\theta(x) = 1$ at $x > 0$), N is the number of points in the initial time series (discretization of the time series should be performed), and r is the size of the phase space partition cell.

The dimension of the attractor d is determined as the slope of the linear portion of the plot of $\ln C(r)$ versus $\ln r$ in a definite r range. At a finite attractor dimension, the $C(r)$ value is saturated.

Figure 4 shows dependences in $\ln C(r)$–$\ln r$ coordinates for successively increasing dimensions of the phase space (n = 2, 3, 4, 5, 6, 7), and Fig. 5 shows the plot of d versus n. Under all conditions, d is saturated, which allows us to state that there exists a deterministic mechanism that controls the oxidation of 1,4-naphthalenediol in the presence of oxygenated cobalt(II) complexes with DMG and Py in the oscillatory mode. The phase space dimension at d is saturated corresponds to 5; i.e., a set of five ordinary differential equations is necessary to describe the patterns of the occurring processes. The attractor dimension has fractional values. These data indicate that, in all cases under consideration, the systems are in the state of dynamic chaos (Table 2).

Calculations of the Lyapunov Characteristic Exponents and the Kolmogorov–Sinai Entropy

There is a fundamental difference in behavior between the systems with regular motion and those with chaotic dynamics: their attractors are different (simple attractors correspond to regular motion, and strange attractors correspond to deterministic chaos) [1, 7]. Dynamic chaos is a result of the instability of phase trajectories (the divergence of close integral curves in the phase space as time elapses). Therefore, the divergence of the phase trajectories of a dynamic system is chosen as the criterion of chaotic motion; i.e., the phase

Table 2. Quantitative characteristics of the dynamics of occurring processes

Conditions	d	λ_1	λ_2	λ_3	h, s^{-1}	t, s
$C_R = 1.5 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	1.90	0.060	0	−0.062	0.060	16.7
$C_R = 2.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	1.95	0.048	0	−0.052	0.048	20.8
$C_R = 2.5 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	2.95	0.044	0	−0.045	0.044	22.7
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	3.90	0.049	0	−0.050	0.049	20.4
$C_R = 3.5 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	3.90	0.071	0	−0.075	0.071	14.8
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 0.75 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	2.20	0.089	0	−0.152	0.089	6.6
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.25 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.96	1.95	0.062	0	−0.069	0.062	16.1
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.77	3.80	0.069	0	−0.079	0.069	14.5
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 7.87	3.70	0.081	0	−0.086	0.081	12.3
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 8.05	3.65	0.066	0	−0.068	0.066	15.2
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 50°C$; pH 8.14	3.85	0.059	0	−0.064	0.059	16.9
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 45°C$; pH 7.96	2.80	0.037	0	−0.039	0.037	27.0
$C_R = 3.0 \times 10^{-3}$; $C_{cat} = 1.00 \times 10^{-4}$ mol/L; $T = 55°C$; pH 7.96	2.30	0.053	0	−0.062	0.053	18.9

trajectory $x(t)$ emerging from the point $x(0)$ and a trajectory close to the first one,

$$x_1(t) = x(t) + \boldsymbol{\varepsilon}(t),$$

are considered.

The consideration of the function

$$\lambda[\boldsymbol{\varepsilon}, 0] = \lim_{t \to \infty} \ln[|\boldsymbol{\varepsilon}(t)|/\boldsymbol{\varepsilon}(0)]$$

defined on the initial displacement vectors in such a manner that $|\boldsymbol{\varepsilon}(0)| = \varepsilon$ at $\varepsilon \longrightarrow 0$ shows that, at all possible rotations of the $\boldsymbol{\varepsilon}(0)$ vector in n directions in the N-dimensional space, the function λ will change jumpwise and adopt a finite number of values $\lambda_1, \lambda_2, \ldots, \lambda_n$. These quantities are referred to as the Lyapunov exponents. They are averaged characteristics of the attractor and describe its properties independently of the initial conditions. Their values allow one to judge the rate of loss of information on the initial state. Dynamic chaos occurs only in dissipative systems and is characterized by the presence of positive Lyapunov exponents in the spectrum.

Another characteristics of the dynamics of occurring processes is the Kolmogorov–Sinai entropy (KS entropy, h), which can be used for determining the type of behavior of a system. The exact value of h is determined by the formula

$$h = \lim_{\substack{d(0) \to 0 \\ t \to \infty}} t^{-1} \ln[d(t)/d(0)].$$

If dynamics is periodic or quasiperiodic, $h = 0$; if the motion is characterized by a stable stationary point, $h < 0$. However, in the case of deterministic chaos ($h > 0$), the KS entropy takes a finite positive value. The characteristic time for which the behavior of the system can be predicted is inversely proportional to the KS entropy. Based of the KS value, the character of oscillations can be estimated not only qualitatively but also quantitatively: the inverse of the entropy $t = h^{-1}$ determines the characteristic time for which the behavior of the system can be predicted. The quantitative relationship between the Lyapunov exponents and KS entropy was found. The KS entropy is related to the positive Lyapunov exponents by the equation

$$h = \sum_{\lambda > 0} \lambda_i.$$

The Lyapunov exponents and KS entropy were calculated for all experimental series with the use of the TISEAN 2.1 freeware program [8]. The results of calculations in the form of a dependence of the Lyapunov exponents on the time series length are shown in Fig. 6; the λ_1, λ_2, λ_3, and h values, as well as the time for which the behavior of the system can be predicted, are presented in Table 2, which shows that, under all experimental conditions, the system is in the state of deterministic chaos ($\lambda_1 > 0$, $\lambda_2 = 0$, $\lambda_3 < 0$, $h > 0$, the attractor

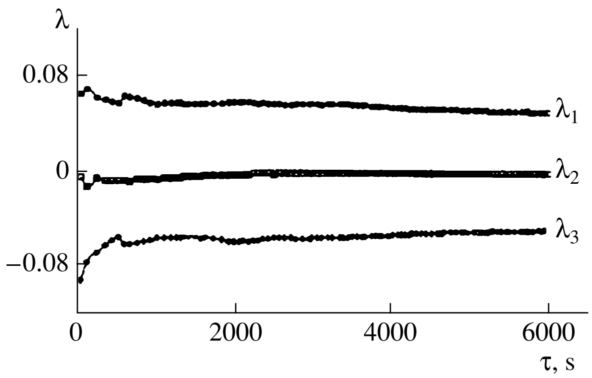

Fig. 6. Lyapunov exponents as a function of the time series length.

has fractional dimensions). Table 2 also shows that the description of the dynamics of the processes based on processing time series by the above methods leads to the same results, which confirms the validity of the approaches to time series analysis used in this work.

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