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Magnetic field effects on chemical reactions near the disturbance of stationary states conditions

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Abstract: The influence of magnetic fields on chemical processes has long been the subject of interest to researchers. For this time numerous investigations show that commonly the effect of a magnetic field on chemical reactions is insignificant with impact less than 10 percent. However, there are some papers that point to the observation of external magnetic field effect on chemical and biochemical systems actually having a significant impact on the reactions. The reason of the effect should be based on searching physically clear processes which mechanisms are well investigated.
The paper theoretically deals with two models explaining how an applied weak magnetic field might influence the steady state of a non-equilibrium chemical system. It is speculated that an applied weak magnetic field might induce a slight change of some rate constants of radical reactions involved in the chemical system. This, in turn, leads to a bifurcation of steady states and implies an abrupt change in temperature and concentration.
Keywords: radicals, recombination, magnetic effects, stationary states, critical phenomena, photochemical system, chain reactions with degenerate branching.

1 Introduction

The influence of magnetic fields on chemical processes has long been the subject of interest to researchers. For this time physically clear notions have been formed of the fact that though the energy of magnetic interactions is small, under certain conditions relatively weak magnetic fields can noticeably affect the rates of chemical reactions with the participation of paramagnetic particles [1-6]. It has been established that the magnetic effect manifests itself in the competition of different channels of conversion in elementary reaction stages, and is determined by the dependence of chemical process effectiveness on the spin state of the pair of the reacting particles, as well as by magnetosensitivity of transitions between spin states (radical pair mechanism) [7-9].
Considerable recent attention has been focused on investigation of weak magnetic fields on chemical and biochemical systems and numerous

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investigations have shown that commonly the effect is insignificant. For example, Brocklehurst and McLauchlan [10] in the model with one magnetic field by numerical methods have obtained approximately 10% change in the reaction rate as compared to geomagnetic field assuming radical pair lifetime equal to $2 \cdot 10^{-7}$ s. Probably, just the value of the order of 1-10% should be considered as quite suitable for the estimation of possible magnetic effects in weak magnetic fields (of the order of geomagnetic field) in chemical and biochemical systems.

However, there are a number of papers that point to the observation of external magnetic field effect on chemical and biochemical systems actually having a significant impact on the reactions. The best known examples of the influence of weak magnetic fields on biological systems are the two established facts: annual migration of birds that orient themselves by magnetic field of the Earth, and the increased number of cancer cases in the regions near retranslating GSM towers.

On the other hand, it is well-known that in non-equilibrium processes even small perturbations can cause essential consequences in non-linear systems where feedbacks play an important role. The reason is the state stability disturbance, and therefore abrupt change of the process regime [11]. One can believe that in some chemical or biochemical systems rather strong influence of weak magnetic fields is also determined by the disturbance of stationary state stability, and transition of the system to another behavior regime [12-16].

Thus the starting point for searching the system where the strong effect of the weak magnetic field is possible is the consideration of chemical systems in the stationary state near the stability conditions violation. First, the reactions with the participation of radical pairs should be considered. It is supposed that under certain conditions external magnetic fields that change the rate constants of processes involving radicals can disturb the stability of stationary states and transfer the system to another stable state considerably differing from the initial one.

The first model system describes dissociation reaction of cyclic ketones under the action of external radiation (laser) which results in biradicals and their subsequent recombination. Non-linear affects in the system are determined by positive reverse relation occurring due to biradical recombination rate dependency of the system temperature and selective absorptance efficiency of the system (absorb only cyclic ketones). The second model system describes hydrocarbon oxidation in liquid phase in presence of inhibitor. The system temperature is considered to be constant and non-linear effects in the system are determined by non-linear kinetic equations describing the system.

Let us remark, that the considered systems are realistic, but rather academic. The real systems are much more complicated and we don't have the goal to describe all effects of weak magnetic fields on chemical and biochemical systems. Although, the supposed approach shows, that in spite of the energy of magnetic interactions is extremely low compared to the energy of chemical bond, the external weak magnetic field in some certain conditions is able to alter system properties dramatically.

2 The Models and Computations

2.1 Photochemical system

The first system under study describes dissociation reaction of cyclic ketones under the action of external radiation (laser) which results in biradicals and their subsequent recombination. The system can exchange energy with reservoir. So, stationary states of the system are determined both by concentration of reactants, and by stationary temperature.

Thus, under the action of external radiation the molecule-precursor A produces biradical B that can subsequently recombine to give the initial molecule

$$A \xrightarrow{\hbar\nu} : B \to A. \tag{1}$$

The kinetic equation defining the concentration change of biradicals B is as follows

$$\frac{dn_B}{dt} = \frac{I_{abs}}{V N_A \hbar\nu} - K(T) n_B, \tag{2}$$

where n_B is biradicals concentration, $K(T)$ is monomolecular recombination rate constant of biradicals B depending on the temperature T of the reacting system, I_{abs} is the energy absorbed by the reacting system per unit time, ν is laser generation frequency, $\hbar$ is the Planck constant, V is the volume of solution excited by laser radiation, N_A is the Avogadro constant.

The first term in the right-hand side of equation (2) describes the production of biradicals due to photolysis. I_{abs} appearing in it is defined using the Buger-Lambert-Beer law on the assumption that at the given laser generation frequency only molecules A (biradicals) absorb

$$I_{abs} = I_0(1 - \exp(-n_A \varepsilon l)). \tag{3}$$

where I_0 – incident radiation power, n_A – substance A concentration, ε – substance A extinction coefficient, l – dishes length with solution.

We accept the following temperature dependence of recombination rate constant [17, 18]

$$K(T) = K_0 \exp\left(-\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right), \tag{4}$$

where T – the reacting system temperature, T_0 – the reservoir temperature that is kept constant, K_0 – the rate constant determined at the temperature T_0, E_A – recombination barrier, R – universal gas constant.

As already mentioned, the internal energy of the system changes due to radiation absorption and loss of heat to the reservoir kept at constant temperature T_0. The mean variation rate of external energy of the system may be written as

$$\frac{dE}{dt} = I_{abs} - \alpha(T - T_0), \tag{5}$$

where α – heat emission coefficient between the reacting system and reservoir, T – the mean temperature of the system.

Note that as laser beam passes through the substance, radiation is absorbed, and the beam intensity decreases. Therefore, generally speaking, the system is inhomogeneous, and one should take into account spatial dependence of internal energy and concentrations. However, for simplicity we take that the intensity of heat and mass exchange inside the reacting system is rather high, and the inhomogeneity is insignificant.

So the evolution of the system in question will be described by differential equations (2) and (5), however, we are interested solely in stationary states of the system defined by the condition

$$\frac{dE}{dt} = \frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dT}{dt} = 0. \tag{6}$$

It is assumed that external magnetic field can change the recombination rate constant $K(T)$ of biradicals B [19-22], and at certain parameters of the system violate the condition of stability of the stationary state thus transferring the system to another stationary state characterized by another values of T, n_A and n_B.

Now we pass to the question concerning the necessary conditions under which multiple stationary states will be observed in the system. It is convenient to consider the situation when the absorptance of substance A is low (i.e., $n_A \varepsilon l << 1$). This essentially simplifies mathematical analysis of the system.

The condition of low absorptance of substance A will be fulfilled at all possible concentrations of substance A, if the initial concentration satisfies the condition

$$n_A^0 \varepsilon l << 1. \tag{7}$$

Based on equations (2), (5) and conditions (6), (7), write the set of equations defining the appearance of stationary states in the system

$$\begin{cases} I_0 n_A \varepsilon l - K(T) n_B V N_A \hbar\nu = 0 \\ I_0 n_A \varepsilon l - \alpha(T - T_0) = 0 \\ n_A^0 = n_A + n_B \end{cases}, \tag{8}$$

where n_A^0 – the initial concentration of substance A. It is assumed that at the initial instant of time the concentration of biradicals B is equal to zero.

For further analysis it is convenient to introduce the following dimensionless quantities

$$x = \frac{E_A}{RT_0} \tag{9}$$

and

$$z = \frac{n_A^0 K_0 V N_A \hbar \nu}{\alpha T_0}. \tag{10}$$

Thus the parameter x defines the value of the activation barrier in biradical recombination reaction with respect to the temperature of reservoir. The parameter z describes the ratio between the rate of the energy delivery to the system and that of the energy expenditure due to the heat loss to reservoir.

The detailed analysis shows that for multiple stationary states to be found in the system, the reacting system parameters z and x must satisfy the relations

$$0 < xz \le \frac{4}{e^2} \tag{11}$$

and

$$x < -\frac{(-1 + W(-ez))^2}{W(-ez)}, \tag{12}$$

where W – the Lambert function.

As x is positive, and the Lambert function W is negative on the interval $[-1/e, 0)$, we have the condition for the value of z

$$0 < z \le \frac{1}{e^2}. \tag{13}$$

The next figure presents dependences (11) and (12). The parameter x is plotted on the abscissa axis, the parameter z - on the ordinate axis. The upper curve corresponds to condition (11), the lower one – to condition (12). At $z = 1/e^2$ both curves merge at the point $x = 4$, with z tending to zero, both curves tend to infinity.

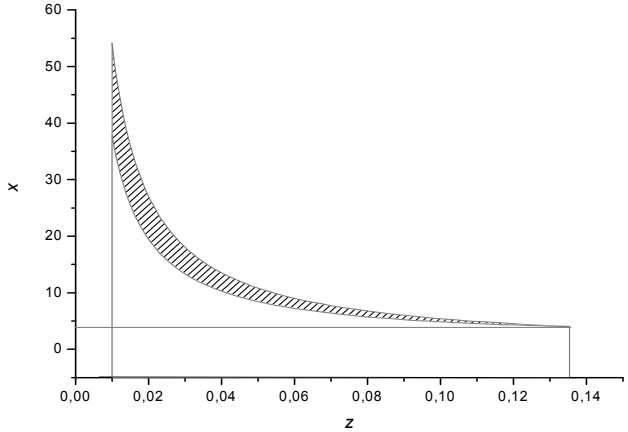

Fig.1. The set of *x* and *z* values (crosshatched region) for which the system has multiple stationary states.

So if the value z fails to satisfy condition (13), then only one stationary state will always exist in the given system, whatever the parameter x. If the parameter z satisfies condition (13), then three stationary states can be found in the system only in case the parameter x satisfies conditions (11) and (12) (i.e., is inside the crosshatched region in Fig.1).

Table 1 shows the parameters of the system used in further calculations. Condition (7) of low absorptance of substance A is not employed. On the one hand, these parameters agree with real values in experiments, and on the other hand, they satisfy conditions (11) and (12).

Parameter	Description	Units	Value
V	volume of solution exposed to radiation	L	$1.27 \cdot 10^{-8}$
l	dish length	cm	0.2
α	heat conductivity	W/K	$1.3 \cdot 10^{-3}$
n_A^0	initial concentration of A substance	mol/L	$5.1 \cdot 10^{-5}$
ε	extinction coefficient of A substance	L/(mol·cm)	$3 \cdot 10^{4}$
E_A	activation barrier of B biradicals recombination	kJ/mol	12.5
T_0	reservoir temperature	K	200
K_0	B biradicals recombination constant at temperature T_0	1/s	10^{5}
ν	exciting radiation frequency	1/s	$6.2 \cdot 10^{14}$
c	velocity of light	m/s	$3 \cdot 10^{8}$
$\lambda = c/\nu$	exciting radiation wave length	Nm	428.6
$\hbar$	Planck constant	J/s	$1 \cdot 10^{-34}$
N_A	Avogadro constant	1/mol	$6 \cdot 10^{23}$
R	universal gas constant	J/(mol·K)	8.31
z	dimensionless parameter	-	0.07
x	dimensionless parameter	-	7.5

Table 1. Parameters used in calculations.

Leaving aside a specific example of biradical and calculation details, for definiteness we take that in experimental conditions biradical lifetime τ_0^m (as a reverse value of $K(T)$) in the presence of magnetic field (of the order of several oersted) differs from biradical lifetime τ_0 in the absence of magnetic field approximately by 10 percent

$$\tau_0^m = 1.1\tau_0 = 1.1 \cdot \qquad (14)$$

For the parameters from Table 1 below we give stationary dependences of the reacting system temperature T and biradical concentration on external radiation value I_0, respectively. Solid line denotes the dependence in the absence of external magnetic field, dotted line – in the presence of magnetic field.

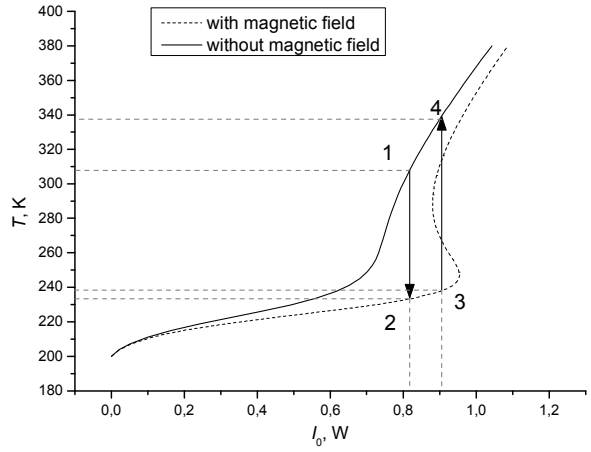

Fig.2. Stationary temperature dependence of the reacting system on external radiation value in the presence and in the absence of magnetic field.

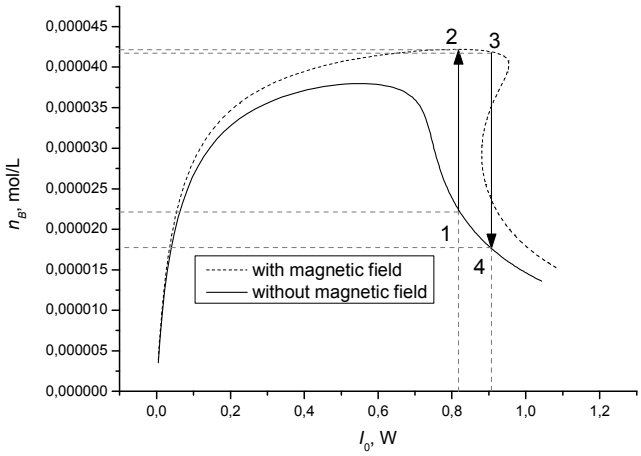

Fig.3. Stationary concentration dependence of biradicals on external radiation value in the presence and in the absence of magnetic field.

2.1 Hydrocarbon oxidation in liquid phase

The second system under study describes hydrocarbon oxidation in liquid phase in presence of inhibitor. The reaction system under discussion is a flow reactor of the volume V to the inlet of which hydrocarbon of concentration $[RH]_0$ is constantly delivered at the rate ω in the mixture with the inhibitor of concentration $[I]_0$ under oxygen saturation conditions; the reaction mixture constantly flows from the chamber at the same rate.
Elementary stages of the reaction are following [23, 24]

$$
\begin{aligned}
&(15.1) \quad RH + O_2 \xrightarrow{k_1} R^{\bullet} \\
&(15.2) \quad R^{\bullet} + O_2 \xrightarrow{k_2} RO_2^{\bullet} \\
&(15.3) \quad RO_2^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet} \\
&(15.4) \quad ROOH \xrightarrow{k_4} 2R^{\bullet}\left(RO^{\bullet} + OH^{\bullet}\right) \\
&(15.5) \quad RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_5} P_1 \\
&(15.6) \quad RO_2^{\bullet} + I \xrightarrow{k_6} P_2
\end{aligned}
\qquad (15)
$$

where I – inhibitor; P_1, P_2 – stable reaction products. Here reaction (15.1) characterizes the process of the chain generation, reactions (15.2) and (15.3) define the chain evolution, reaction (15.4) – decay into radicals (degenerate chain branching), reactions (15.5) and (15.6) – chain termination. Characteristic rate constant values of the corresponding processes are given in Table 2.

Parameter	Value	Units
k_1	$5 \cdot 10^{-17}$	L/mol·sec
k_2	$2.7 \cdot 10^{6}$	L/mol·sec
k_3	0.13	L/mol·sec
k_4	$5.6 \cdot 10^{-10}$	1/ sec
k_5	$2.8 \cdot 10^{6}$	L/mol·sec
k_6	$2 \cdot 10^{6}$	L/mol·sec

Table 2. Rate constants of elementary stages processes (2).

The kinetic equations describing the change in reactants concentration in the reaction system are

$$\begin{cases} \dfrac{dx_1}{dt} = k_1 yg - k_2 x_1 g + k_3 y x_2 + 2k_4 x_3 - \upsilon x_1 \\ \dfrac{dx_2}{dt} = k_2 x_1 g - k_3 x_2 y - 2k_5 x_2^2 - k_6 x_2 z - \upsilon x_2 \\ \dfrac{dx_3}{dt} = k_3 x_2 y - k_4 x_3 - \upsilon x_3 \\ \dfrac{dz}{dt} = -k_6 z x_2 + \upsilon z_0 - \upsilon z \\ \dfrac{dy}{dt} = -k_1 yg - k_3 x_2 y + \upsilon y_0 - \upsilon y \end{cases}, \tag{16}$$

with the following designations: $x_1 = [R^{\bullet}]$, $x_2 = [RO_2^{\bullet}]$, $x_3 = [ROOH]$, $y = [RH]$, $y_0 = [RH]_0$, $z = [I]$, $z_0 = [I]_0$, $g = [O_2]$ and $\upsilon = \omega / V$.

As is known, the external magnetic field is able to affect the elementary event rate of radical pair recombination in liquids (the model of radical pairs). Among the elementary stages presented in scheme (15), only reactions (15.4) and (15.5) proceed with radical pairs, therefore, only they can be subjected to external magnetic field.

It is assumed that external magnetic field can affect recombination rate constants k_4, k_5, and violate the stability of a steady state (at certain parameters of the system) thus transferring the system to another steady state essentially differing from the initial one.

Now considerable attention has been given to finding the stationary states possible in the system, and defined by the conditions

$$\frac{dx_1}{dt} = \frac{dx_2}{dt} = \frac{dx_3}{dt} = \frac{dz}{dt} = \frac{dy}{dt} = 0 . \tag{17}$$

Let us assume that hydrocarbon concentration inside the reactor is equal to its initial concentration delivered to the reactor inlet, e.g., it is kept constant

$$y = y_0 . \tag{18}$$

The assumption seems to be valid, since the initial concentration is rather high, and reactions (15.1), (15.2) and (15.3) can be neglected. Initial concentration of the inhibitor is rather small (as is seen from typical conditions of experiments of this kind), and so processes with its participation could not be neglected [25-28]. The approach essentially simplifies further mathematical examination of system (16), and allows one to obtain a cubic equation for stationary peroxide radical concentration

$$x_2^3 + a_1 x_2^2 + a_2 x_2 + a_3 = 0 , \tag{19}$$

where the corresponding coefficients are

$$a_1 = \frac{1}{2k_5k_6}\left(\upsilon(2k_5+k_6)+k_3k_6y-\frac{k_2k_3k_6g\,y}{k_2g+\upsilon}\left(1+\frac{2k_4}{k_4+\upsilon}\right)\right),$$
$$a_2 = \frac{1}{2k_5k_6}\left(\upsilon(\upsilon+k_3y+k_6z_0)-\frac{k_2k_3g\,\upsilon\,y}{k_2g+\upsilon}\left(1+\frac{2k_4}{k_4+\upsilon}\right)-\frac{k_1k_2k_6g^2y}{k_2g+\upsilon}\right), \quad (20)$$
$$a_3 = -\frac{k_1k_2g^2\upsilon\,y}{2k_5k_6(k_2g+\upsilon)}.$$

The third power of equation (20) for stationary radical concentration indicates that for constant external parameters of the system, three stationary states with different concentrations of reactants can exist. The condition of three real roots of the equation is defined as follows

$$a_1^2a_2^2-4a_1^3a_3-4a_2^3+18a_1a_2a_3-27a_3^2>0,$$
$$a_1^2-3a_2>0. \quad (21)$$

According to the Descartes theorem, all roots of the equation written as (20) are positive if and only if its consistent coefficients are of opposite sign, i.e.

$$a_1<0,\quad a_2>0,\quad a_3<0. \quad (22)$$

In Table 3 represents system parameters and elementary rate constants which were fitted close to the established ones in experiments of hydrocarbons in the liquid phase under oxygen saturation conditions so as to satisfy conditions (21) and (22). Assumption (18) concerning constant hydrocarbon concentration inside the reactor is not used.

Parameter	Value	Units
$[O_2]$	10^{-3}	mol/L
$[RH]_0$	5	mol/L
υ	$1\cdot10^{-6}$	1/sec

Table 3. System parameters.

Taking into account actual values of recombination rate constants k_4 and k_5 (see Table 2), we assume that only recombination rate constant of peroxide radicals could be affected by external magnetic field [29]. Leaving aside a specific example of the radical, we assume the magnetic field effect to be 10%.

Following figure shows two stationary concentrations of peroxide radicals as a function of inhibitor concentration delivered into the reactor in the presence and in the absence of external magnetic field (solid line denotes the dependence in the absence of external magnetic field, dotted line – in the presence of magnetic field).

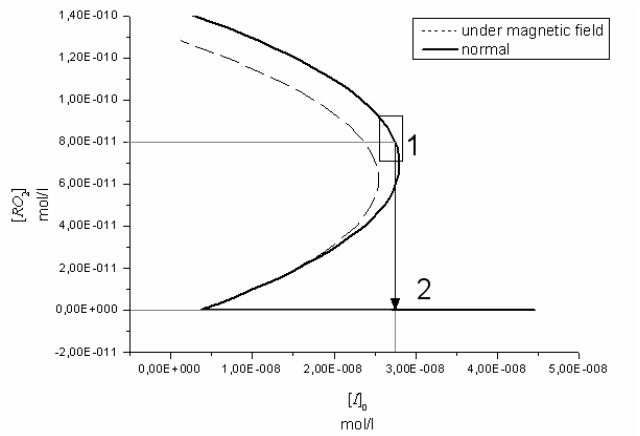

Fig. 4. The dependence of stationary concentration of peroxide radicals on the concentration of inhibitor delivered into the reactor in the presence and in the absence of external magnetic field.

3 Conclusions

External magnetic field affects on rate constants of reactions with paramagnetic particles. Though these effects are rather insignificant, they are responsible for the fact that in the system under study the set of stationary states in the absence of external magnetic field does not coincide with the set of stationary states in the presence of magnetic field. These distinctions are most noticeable in bistability region.

Consider photochemical system more carefully. The external radiation power I_0 is the control parameter. It is seen that at certain values of the control parameter there exist critical points: 0.88 W and 0.96 W. These are bifurcation points, since with increasing (or decreasing) laser power the number of stationary states changes abruptly – depending on laser radiation intensity I_0 stationary states with one or three different values of the reacting system temperature can be observed. At the parameter values slightly higher (or slightly lower) than the critical value the state is stable. In degeneration region of stationary states only stationary states lying between the curve maxima and minima (Fig.2) are asymptotically unstable.

Two characteristic regions can be distinguished where great effect of weak magnetic field on the system is noted: at the values of I_0 from 0.74 W to 0.88 W, and from 0.88 W to 0.96 W. Examine the behavior of the system at external radiation power 0.81 W. In the absence of magnetic field the reacting system is in the stationary state characterized by stationary temperature about 308 K. In the presence of magnetic field this stationary state becomes unstable, and at the given radiation power the system abruptly changes to high temperature branch, and to another stationary state with the temperature about 232 K. Now consider

the second region, i.e., the external radiation power is 0.92 W. Let the magnetic field be present, then the reacting system will have the stationary temperature about 238 K. Switching off the magnetic field will make this stationary state unstable, and the system will abruptly go to another stationary state with the temperature about 344 K. This will lead to intensive heating of the system. As is seen from Fig.3, the change in stationary temperature will be accompanied by an abrupt change in stationary concentrations of reactants.

Analogous magnetic field effect could be observed in system described hydrocarbon oxidation in liquid phase (see Fig.4). To reveal the essence of the effect, examine the behavior of the system at the inhibitor concentration $[I]_0 = 2{,}7 \cdot 10^{-8}$ mol/L. Let the system be in a steady state which corresponds to point 1 in the diagram. This steady state is stable, and concentration of peroxide radicals is $[RO_2^{\bullet}] = 8 \cdot 10^{-11}$ mol/L. Switching on the external magnetic field violates the stability condition of this state, and the system is to change to another branch of steady states. Thus with constant $[I]_0$ the system goes to another steady state under the action of external magnetic field. This state (point 2 in the diagram) will be characterized by another stationary concentration $[RO_2^{\bullet}] = 1 \cdot 10^{-17}$ mol/L of peroxide radicals.

So the possibility of strong effect of weak magnetic fields of the order of several oersted in the considered systems is theoretically predicted. External magnetic field may be responsible for the violation of the stationary state stability condition, and change radically the system properties. It is similar to the phase transition of the first kind, and will be accompanied by intensive heating (cooling) of the system, and abrupt change in concentrations of reacting substances.

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