THE AUTOCATALYTIC REDUCTION OF FERRIIN BY MALONIC ACID WITH REGARD TO THE FERROIN-CATALYZED BELOUSOV–ZHABOTINSKY REACTION[+]

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Dedicated to Professor Miroslav Urban on the occasion of his 60th birthday.

The reduction of ferriin ($[Fe(phen)_3]^{3+}$, phen = 1,10-phenanthroline) by malonic acid (MA) differs from the reduction of Ce(IV) or Mn(III) ions by MA in its autocatalytic character and in a pregnant influence of oxygen, which behaves obviously as a catalyst. The time dependence of the ferroin–ferriin redox potential at the last stage of this reaction has a sigmoidal shape, which indicates autocatalysis. Under anaerobic conditions, the inflection time is of the order of several tens of minutes, since autocatalysis cannot proceed unless a sufficient amount of oxygen is produced *via* oxidation of water (OH^- ions) with Fe(IV) formed by the ferriin dismutation. Under aerobic conditions, the inflection time decreases to a value of a few seconds. The probable reaction mechanism is discussed in detail.
Keywords: Ferriin reduction; Malonic acid; Ferroin redox catalyst; Belousov–Zhabotinsky reaction; Autocatalytic reaction; Oxygen influence; Oscillatory reactions; Iron.

The Belousov–Zhabotinsky reaction (BZR), discovered in 1958, has atracted much attention and is probably the most thoroughly investigated oscillatory reaction at present. The BZR, especially with the ferroin–ferriin redox catalyst, is of great importance, since the ferroin-catalyzed BZ systems are used very often for experiments with spatial pattern formation. Although,

in general, some real progress has been made toward the understanding of the complex kinetics involved in the BZR, less work has been done on the kinetics of the ferroin-catalyzed oscillations.

The oxidation of ferroin with bromate is autocatalytic[1], if $[Fe(phen)_3]^{2+} \ll [BrO_3^-]$. Smoes[2,3], who declared it to be still underinvestigated, studied the oscillations in the ferroin-catalyzed BZ system in detail. Trigger waves in the acid bromate oxidation of ferroin were studied by Showalter[4], which assumed them to provide strong support for the Field–Noyes mechanism[5]. The reduction of ferriin with a substrate has been studied especially in the case of bromomalonic acid[6,7]. Rovinsky and Zhabotinsky have proposed[7] for this reaction a mechanism involving eleven steps and the corresponding mathematical model was reduced to a second-order system of differential equations, which seems to be in good agreement with experiment. Rovinsky[8] has succeeded in proving that this model leads to the Turing bifurcation and stationary patterns. Jwo *et al.*[9] studied the ferriin oxidation of malonic acid and its derivatives. They have found that the order of relative reactivities in ferriin oxidation depends on whether anaerobic or aerobic conditions are used.

We have described[10,11] the oxygen-induced excitability with the ferroin-catalyzed BZR if ethyl 3-oxobutanoate is used as a substrate. It is remarkable that the time dependence of the ferroin concentration has a non-monotonic character in the course of the reaction between $Ce(SO_4)_2$ and ferroin in dilute sulfuric acid[12]. The proposed mechanism is based on the existence of tetravalent iron that is one of the products of ferriin dismutation. The ferroin-catalyzed BZ oscillatory system with methyl, ethyl, or isopropyl ester of 3-oxobutanoic acid exhibits "clock" behaviour and subsequent two-frequency oscillations[13]. The influence of oxygen on the "clock" behaviour is assumed to be caused by interaction of oxygen as a scavenger with intermediate radicals.

EXPERIMENTAL

Materials and Measurements

Stock solutions of the components were prepared from commercially available chemicals. The solutions of ferriin sulfate were prepared by electrooxidation of ferroin sulfate in 3 M H_2SO_4 on platinum macroelectrodes (Winkler electrodes) under a nitrogen atmosphere for 45 min.

The reaction course was followed potentiometrically, by recording the time dependence the ferroin–ferriin redox potential (with a platinum electrode) against the potential of the $Hg/Hg_2SO_4/1$ M H_2SO_4 reference electrode. The dependences were monitored with a digital multimeter METEX, M 4650CR connected to a PC 386 computer. The collected data were

elaborated using the programs Gnuplot and Excel. The experiments were performed in a closed stirred thermostatted glass reactor at 20 °C.

The reaction solution was stirred at 200 rpm with a magnetic stirrer. The concentration of oxygen was determined using an oxygen-sensitive combined electrode, type RA-0950P (Radelkis, Hungary).

Spectrophotometric measurements were performed using a Specord M 40 spectrophotometer (Carl Zeiss, Jena) and 1-cm quartz cuvette with a mantle connected to ultrathermostat U 15 (Germany).

RESULTS AND DISCUSSION

If the kinetics of the ferriin reduction with malonic acid (MA) in 2×10^{-1} M sulfuric acid is followed potentiometrically, a sigmoidal time dependence of the ferroin–ferriin redox potential is observed, indicating an autocatalytic character of either the whole process or a reaction step involved in the reduction process (Fig. 1). The first part of the ferriin reduction proceeds monotonically, at least from its initial 1×10^{-4} to 5×10^{-6} mol l^{-1} concentration, following the first-order kinetics, as described in ref.[9] The final stage of the reaction has evidently an autocatalytic character, since the $E = f(t)$ curve obtains a sigmoidal shape. If we compare the curve with those corresponding to the reduction of Ce(IV) or Mn(III) ions by MA at the same initial concentrations of the components, the difference is obvious. The potential of the Ce(III)/Ce(IV) or Mn(II)/Mn(III) redox couples tends to reach
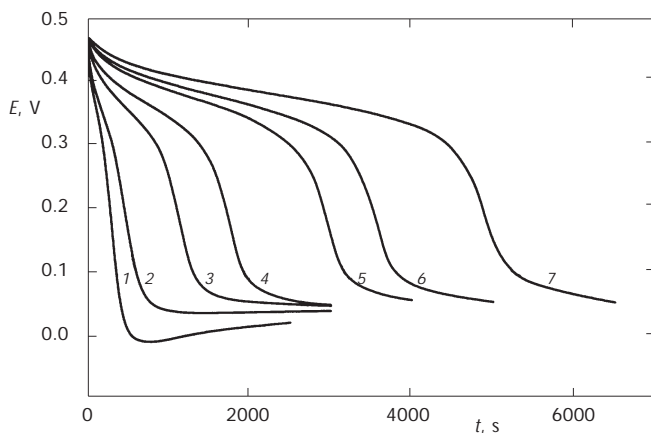

FIG. 1
Sigmoidal character of the $E = f(t)$ curves at the final stage of the BZ reaction at 20 °C. Initial conditions: $[H_2SO_4]_0 = 0.2$ mol l^{-1}; $[ferriin]_0 = 0.103$ mmol l^{-1}; $[MA]_0 = 0.4$ (*1*), 0.3 (*2*), 0.1 (*3*), 0.05 (*4*), 0.02 (*5*), 0.015 (*6*), 0.01 (*7*) mol l^{-1}

a maximum in a few seconds and then it decreases by the first-order kinetics.

Inflection time (IT) in the system under study decreases with increasing MA concentration (Table I). By logarithmic analysis we get the reaction order of 0.7, $k_{exp} = 1/IT = k$ [ferriin] $[MA]^{0.7}$, indicating the Michaelis–Menten mechanism which is quite frequent for the Ce(IV) oxidations of organic substrates. The value k_{exp} represents the experimental *brutto* rate constant of the autocatalytic reaction. Reducing the initial concentration of ferriin from 1.7×10^{-4} to 1×10^{-5} mol l^{-1} in the same system, inflection time and its slope decrease (Fig. 2).

The IT remarkably increases if oxygen is successively replaced by bubbling nitrogen gas (Fig. 3). Thus, due to the pronounced effect, oxygen is assumed to play the role of an autocatalyst. If air is removed from the solution with a stream of nitrogen, a sufficient amount of oxygen must be accumulated for the reduction of ferriin with MA to proceed faster than in its absence. In 0.2 M H_2SO_4 the dismutation of ferriin can proceed[11] as follows (Eq. (*1*)):

$$2 \; [Fe(phen)_3]^{3+} \; \rightleftharpoons \; [Fe(phen)_3]^{2+} + [Fe(phen)_3]^{4+}. \tag{1}$$
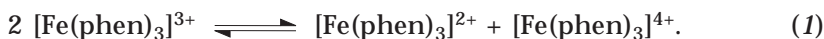
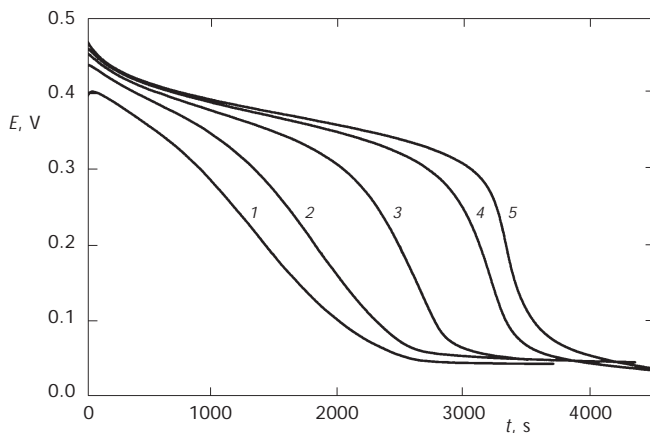Noyes *et al.*[14,15] considered in the frame of the Field–Körös–Noyes (FKN) mechanism other reactions instead of (*2*) and (*3*)
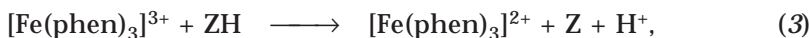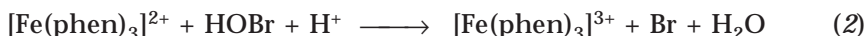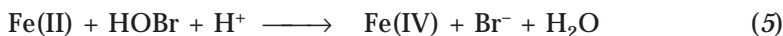
F_IG. 2

Dependence of the inflection time and the slope of its tangent on the ferriin concentration at 20 °C. Initial conditions: $[H_2SO_4]_0 = 0.2$ mol l^{-1}; $[MA]_0 = 0.02$ mol l^{-1}; $[ferriin]_0 = 0.1 \times 10^{-4}$ (*1*), 0.125×10^{-4} (*2*), 0.5×10^{-4} (*3*), 1.33×10^{-4} (*4*), 1.7×10^{-4} (*5*) mol l^{-1}

$$[Fe(phen)_3]^{2+} + HOBr + H^+ \longrightarrow [Fe(phen)_3]^{3+} + Br + H_2O \qquad (2)$$

$$[Fe(phen)_3]^{3+} + ZH \longrightarrow [Fe(phen)_3]^{2+} + Z + H^+, \qquad (3)$$

where ZH denotes an organic substrate. Since reactions (*2*) and (*3*) are thermodynamically not favoured, the authors considered an alternative mechanism with the reactions (*4*)–(*6*).

$$2\ Fe(III) \rightleftharpoons Fe(IV) + Fe(II) \qquad (4)$$

$$Fe(II) + HOBr + H^+ \longrightarrow Fe(IV) + Br^- + H_2O \qquad (5)$$

$$Fe(IV) + ZH + H_2O \longrightarrow Fe(II) + ZOH + 2\ H^+ \qquad (6)$$

Since the value of E^0 for the Fe(IV)/Fe(II) system is equal to 1.2–1.3 V, the last two steps are probable, although the equilibrium (*4*) is shifted too much to the left side to be observable.

The species $[Fe(phen)_3]^{4+}$ (reaction (*1*)) and/or their aquation products $[Fe(phen)_2(H_2O)_2]^{4+}$ as intermediates, denoted as Fe(IV), oxidize water molecules (OH$^-$ ions), probably in a subsequent step
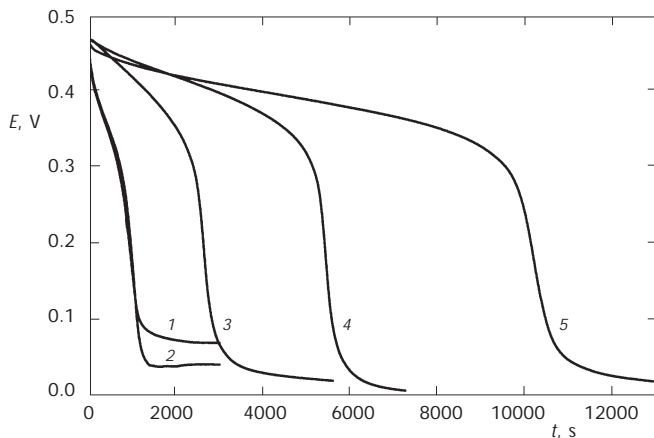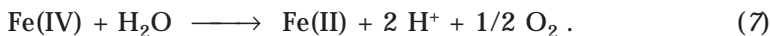

Fig. 3
Dependence of the inflection time on the oxygen concentration at 20 °C. Initial conditions: $[H_2SO_4]_0 = 0.2$ mol l^{-1}; $[ferriin]_0 = 0.103$ mmol l^{-1}; $[MA]_0 = 0.1$ mol l^{-1}; $[O_2]_0 = 1.2 \times 10^{-3}$ (*1*), 2.4×10^{-4} (*2*), 1.48×10^{-4} (*3*), 0.53×10^{-4} (*4*), almost 0 (*5*) mol l^{-1}

$$\text{Fe(IV)} + \text{H}_2\text{O} \longrightarrow \text{Fe(II)} + 2\ \text{H}^+ + 1/2\ \text{O}_2 \ . \tag{7}$$

The sum of reactions (*1*) and (*7*) gives the stoichiometric equation (*8*) of the process.

$$4\ [\text{Fe(phen)}_3]^{3+} + 2\ \text{H}_2\text{O} \rightleftharpoons 4\ [\text{Fe(phen)}_3]^{2+} + \text{O}_2 + 4\ \text{H}^+ \tag{8}$$

(The reduction of ferriin in the absence of MA does proceed, but with a much longer IT than in its presence, as demonstrated hereinafter.)

If the same reaction is followed spectrophotometrically at 509 nm, a non-linear increase tending to a maximum, and then a decrease in the absorbance corresponding to ferroin, can be observed (Fig. 4). This has been described by Jwo *et al.*[9], who proposed a mechanism involving aquation of the $[\text{Fe(phen)}_3]^{3+}$ and $[\text{Fe(phen)}_3]^{2+}$ species.

For the autocatalytic reduction of ferriin with MA (process (*15*)) the following reaction scheme can be proposed:
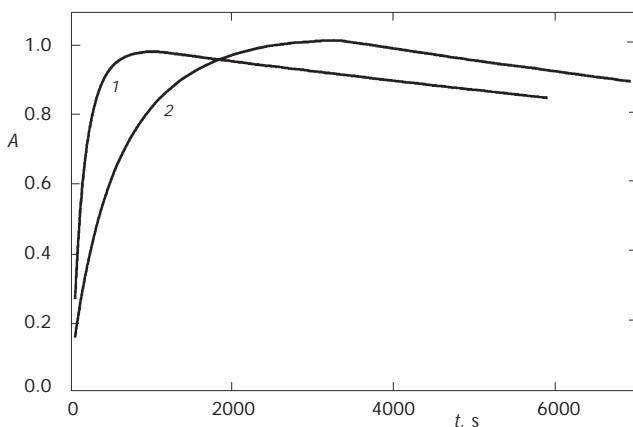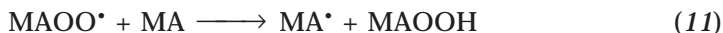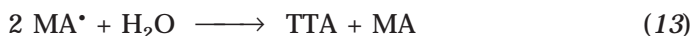
$$[\text{Fe(phen)}_3]^{3+} + \text{MA} \longrightarrow [\text{Fe(phen)}_3]^{2+} + \text{MA}^\bullet + \text{H}^+ \tag{9}$$

$$\text{MA}^\bullet + \text{O}_2 \longrightarrow \text{MAOO}^\bullet \tag{10}$$

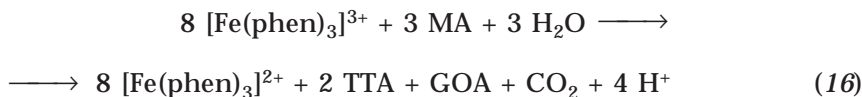$$\text{MAOO}^\bullet + \text{MA} \longrightarrow \text{MA}^\bullet + \text{MAOOH} \tag{11}$$

FIG. 4

Absorbance *versus* time curves at 20 °C and wavelength = 509 nm. Initial conditions: $[\text{H}_2\text{SO}_4]_0$ = 0.2 mol l^{-1}; $[\text{ferriin}]_0$ = 0.103 mmol l^{-1}; $[\text{MA}]_0$ = 0.1 (*1*), 0.02 (*2*) mol l^{-1}

$$[Fe(phen)_3]^{3+} + MAOOH \longrightarrow [Fe(phen)_3]^{2+} + MAOO^\bullet + H^+ \qquad (12)$$

$$2\ MA^\bullet + H_2O \longrightarrow TTA + MA \qquad (13)$$

$$2\ MAOO^\bullet \longrightarrow GOA + TTA + O_2 + CO_2\ , \qquad (14)$$

where $MA^\bullet$ denotes malonyl radical, $MAOO^\bullet$ peroxymalonyl radical, TTA tartronic (oxomalonic) acid and GOA glyoxylic acid. The sum of these reactions gives the stoichiometric equation of the process (*15*).

$$4\ [Fe(phen)_3]^{3+} + 3\ MA + O_2 + H_2O \longrightarrow$$

$$\longrightarrow 4\ [Fe(phen)_3]^{2+} + 2\ TTA + GOA + CO_2 \qquad (15)$$
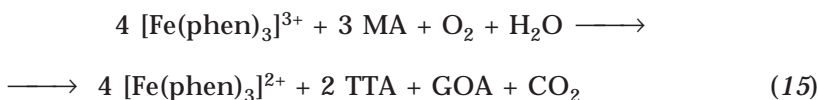
The sum of the processes (*8*) and (*15*) gives a *netto* stoichiometry (*16*).

$$8\ [Fe(phen)_3]^{3+} + 3\ MA + 3\ H_2O \longrightarrow$$

$$\longrightarrow 8\ [Fe(phen)_3]^{2+} + 2\ TTA + GOA + CO_2 + 4\ H^+ \qquad (16)$$

The process (*15*) cannot fully proceed, unless a sufficient amount of oxygen is formed in the process (*8*). Oxygen formed in the process (*8*) is successively consumed in the process (*15*). As we can see, in the *netto* stoichiometric equation (*16*) oxygen is not present, as it behaves as an autocatalyst. Under aerobic conditions, the proccess (*15*) is accelerated by air oxygen and inlection time decreases.

We cannot exclude that in addition to MA oxidation with ferriin, it can also proceed with Fe(IV) species, formed by disproportionation of ferroin (*1*), in a competition reaction:

$$Fe(IV) + MA \rightleftharpoons Fe(IV){-}MA \longrightarrow Fe(II) + products. \qquad (17)$$

The process (*17*) *via* the Fe(IV)–MA intermediate complex, similarly to proces (*3*), may cause the Michaelis–Menten kinetics (Table I).

Thus, we can apply the oxidation mechanism of MA with Ce(IV) according to Barkin *et al.*[16], which seems to be applicable also to the oxidation of MA with Mn(III)[17]. Contrary to those cases, the reduction of $[Fe(phen)_3]^{3+}$ ions with MA at later stages is autocatalytic; the whole process is much more influenced by oxygen than in the previous cases[16,17], which may be due to a much faster reaction step (*12*) compared to (*9*). The accelerating

effect of oxygen on the oxidation of malonic acid with Ce(IV) was studied by Noyes and co-workers[12] and explained by the formation of organic peroxy radicals, which increases the rate of the initial attack on MA. Neumann *et al.*[18] presented electron paramagnetic resonance (EPR) evidence that peroxymalonyl radicals are actually formed in the aerobic oxidation of MA with ceric ions.

The decrease in the inflection time and its slope with decreasing the intial ferriin concentration may be related to the reversibility of the reaction of ferriin with malonic acid which was confirmed by Jwo *et al.*[9] and independently by Muller *et al.*[19]:

$$[Fe(phen)_3]^{3+} + MA \rightleftharpoons [Fe(phen)]^{2+} + MA^\bullet + H^+. \tag{18}$$
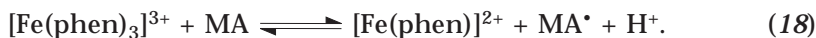
With increasing H_2SO_4 concentration, the inflection time of the ferriin reduction with MA increases, the sigmoidal curve splits into two parts and, finally, in its second part a minimum appears, which becomes more pronounced (Fig. 5). The plot of the reciprocal value of the inflection time *vs* the reciprocal value of the H_2SO_4 concentration is linear (Fig. 6), indicating that HSO_4^- ions probably replace phenantroline as ligand in the coordination sphere and inhibit the reaction.

The inflection time as well as the slope of the tangent in the inflection point increase with temperature according to the Arrhenius equation (Fig. 7). From the former temperature dependence we obtained the energy of activation $E_a = 86.9$ kJ mol^{-1}, and from the latter the value $E_a = 87.7$ kJ mol^{-1}.

TABLE I
Dependence of the inflection time on malonic acid concentrations at 20 °C. Initial conditions: $[H_2SO_4]_0 = 0.2$ mol l^{-1}, $[ferriin]_0 = 0.103$ mmol l^{-1}

$[MA]_0$, mol dm^{-3}	IT, s	$[MA]_0$, mol dm^{-3}	IT, s
0.005	7382	0.2	622
0.01	4866	0.25	542
0.015	3637	0.3	429
0.02	2928	0.4	375
0.05	1732	0.5	284
0.1	1107		

The subsystem, consisting of the ferriin (with traces of ferroin) in 0.2 M H_2SO_4, also undergoes the autocatalytic reduction of ferriin (process (*8*)) with the inflection time of almost 18 h, independently of whether oxygen is present or not, if proceeding in the dark. If the subsystem is illuminated with visible light, inflection time decreases, more in the presence of oxygen
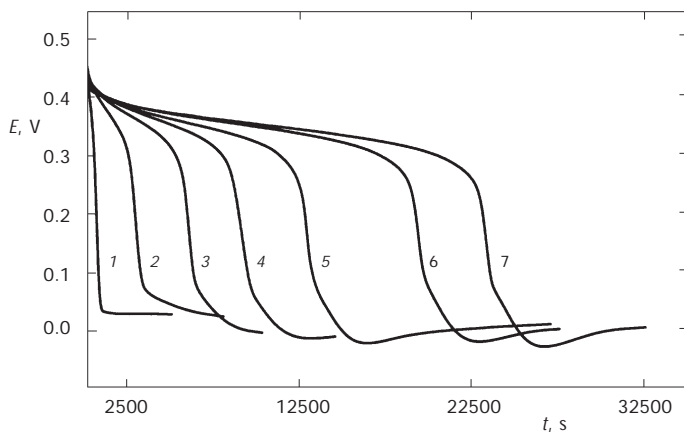

FIG. 5
Dependence of the inflection time on the sulfuric acid concentration at 20 °C. Initial conditions: $[MA]_0 = 0.02$ mol l^{-1}; $[ferriin]_0 = 0.103$ mmol l^{-1}; $[H_2SO_4]_0 = 0.05$ (*1*), 0.2 (*2*), 0.35 (*3*), 0.5 (*4*), 0.7 (*5*), 0.85 (*6*), 1.0 (*7*) mol l^{-1}
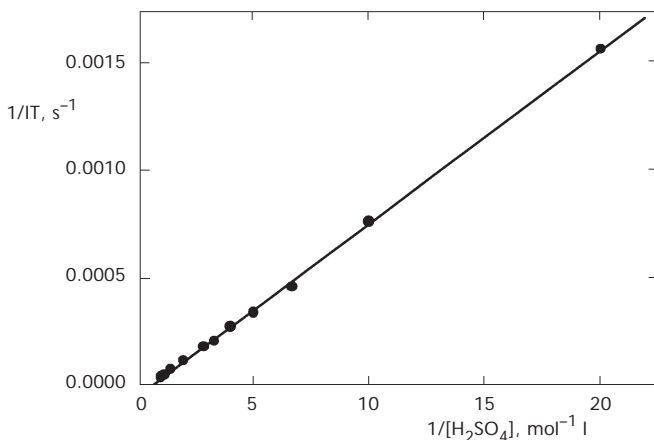

FIG. 6
Dependence of the reciprocal value of the inflection time on the reciprocal value of the sulfuric acid concentration at 20 °C. Initial conditions: $[MA]_0 = 0.02$ mol l^{-1}, $[ferriin]_0 = 0.103$ mmol l^{-1}

than in its absence (Table II). Flash photolysis study of the ferriin ion[20] indicated that the main product of its photolysis in dilute sulfuric acid is the ferroin ion. The quantum yield was less than 1×10^{-4} upon irradiation into the visible absorption band ($\lambda_{max} = 602$ nm) that corresponds to a spin-allowed ligand (π)-to-metal (d_π) charge transfer transition.

The value of the inflection time as a function of temperature has an Arrhenius character. We have evaluated it using the Eyring equation and obtained the corresponding activation parameters (Table III). Comparing

TABLE II
Inflection time in the absence and presence of MA under anaerobic and aerobic conditions at 20 °C. Influence of day light; [ferriin] = 0.114 mmol l^{-1}, [H_2SO_4] = 0.2 mol l^{-1}

Inflection time	Anaerobic conditions		Aerobic conditions	
	dark	day light	dark	day light
IT^a, h	17.98	15.05	17.85	12.04
IT^b, h	1.47	1.12	0.28	0.28

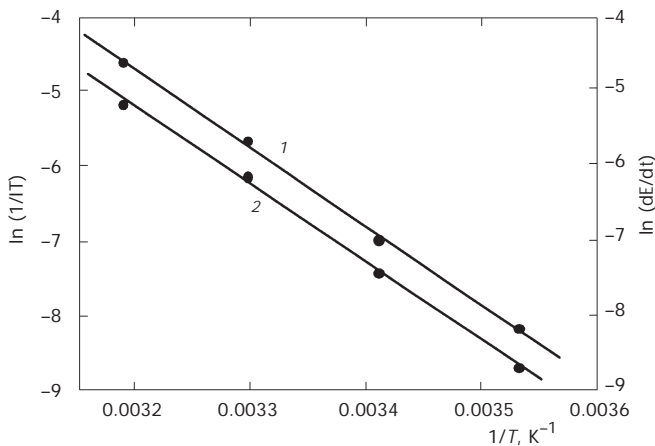^{a} [MA] = 0; ^{b} [MA] = 0.02 mol l^{-1}.

FIG. 7
Dependence of the logarithm of the reciprocal value of the inflection time, ln (1/IT) (*1*), and of the logarithm of the slope of the tangent in the inflection point, ln (dE/dt) (*2*), on the reciprocal temperature. Initial conditions: [MA]$_0$ = 0.02 mol l^{-1}, [ferriin]$_0$ = 0.103 mmol l^{-1}, [H_2SO_4]$_0$ = 0.2 mol l^{-1}

their values under the same conditions, but in the presence of MA, we could not observe any difference in the values of enthalpy of activation, but we observed different values of entropy of activation. The almost four-times enhanced value of entropy of activation in the presence of MA is very significant. Although we do not know activation parameters of elementary reaction steps, the experimental (*brutto*) values of entropy of activation may reflect a great configuration change going from the initial state to the transition state of the reaction.

Chou *et al.*[9] have proposed a mechanism of the ferriin oxidation of MA and its derivatives which includes the reduction of ferriin with $[Fe(H_2O)_6]^{2+}$ formed by aquation. Therefore, we attempted to explain the autocatalytic character of the ferriin reduction (both in the absence and in the presence of MA) alternatively, as the reduction of ferriin with $[Fe(H_2O)_6]^{2+}$ ions formed in traces by aquation of ferroin. In the presence of MA, the

TABLE III
Activation parameters in the absence[a] and presence[b] of MA. [ferriin] = 0.114 mmol l^{-1}, [H$_2$SO$_4$] = 0.4 mol l^{-1}

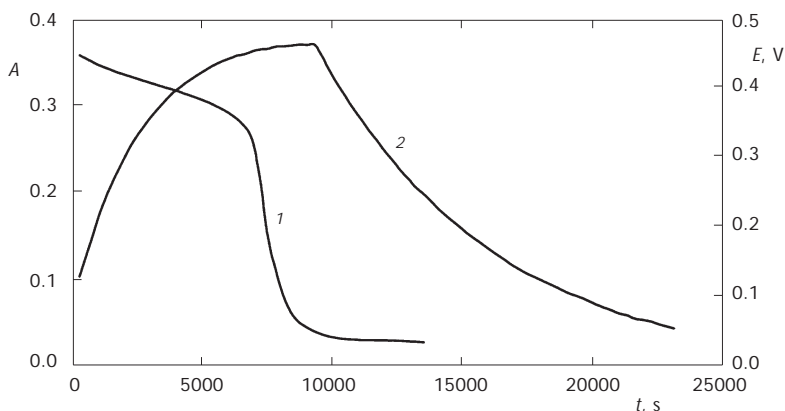| $\Delta H^{\neq}$, kJ mol^{-1}		$\Delta S^{\neq}$, kJ mol^{-1}	
101.6[a]	108.4[b]	9.8[a]	39[b]

[a] [MA]$_0$ = 0; [b] [MA]$_0$ = 1 mol l^{-1}.

FIG. 8
Comparison of the $E = f(t)$ (*1*) and $A = f(t)$ (*2*) curves of the same reaction system at 30 °C. Initial concentrations: [ferriin]$_0$ = 0.114 mmol l^{-1}, [MA]$_0$ = 1 mmol l^{-1}, [H$_2$SO$_4$]$_0$ = 0.4 mol l^{-1}

$[Fe(H_2O)_6]^{2+}$ ions may have been acumulated much faster than in its absence, and the sigmoidal shape of $E = f(t)$ curves described above may have been caused by the final reduction of ferriin with the $[Fe(H_2O)_6]^{2+}$ ions formed by aquation.

For this purpose, we have compared the $E = f(t)$ (*1*) and $A = f(t)$ (*2*) curves of the same system at 30 °C (Fig. 8). We can see that the value of IT is by 32 min lower on the first curve than the start of the ferroin concentration decrease on the second curve. At 20 °C this difference is still larger. Although the aquation of ferroin is evident, the sigmoidal shape of the $E = f(t)$ curves in the last phase of the BZ reaction under study seems to be better explained by our mechanism than that of Chou *et al.*[9]

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