Belousov—Zhabotinskii reaction with esters of 3-oxobutanoic acid

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The kinetics of oxidation of several esters of 3-oxobutanoic acid by Ce(IV) ions in a solution of sulfuric acid was studied. The values of the rate constant k_2, corresponding to the rate equation $v = k_2$ [Ce(IV)] [ester], correlate with the values of substituent constants σ^* in the sense of Taft equation.

On the basis of our kinetic measurements of the Belousov—Zhabotinskii reaction with esters of 3-oxobutanoic acid, we can conclude that some its parameters (the averaged frequency of oscillations and the averaged period of oscillations) also correlate with the values of substituent constants σ^* in the sense of Taft equation.

Изучена кинетика окисления нескольких эфиров 3-оксомасляной кислоты ионами Ce(IV) в растворе серной кислоты. Величины константы скорости k_2, отвечающей уравнению $v = k_2$ [Ce(IV)] [эфир], коррелировали со значениями констант заместителей σ^* в смысле уравнения Тафта.

На основании полученных результатов кинетических измерений реакции Белоусова—Жаботинского с эфирами 3-оксомасляной кислоты можно сделать вывод, что некоторые ее параметры (усредненная частота осцилляций и усредненный период осцилляций) также коррелируют со значениями констант заместителей σ^* в смысле уравнения Тафта.

The ethyl ester of 3-oxobutanoic acid is a very convenient substrate for the Belousov—Zhabotinskii (BZ) reaction because no carbon dioxide is liberated in the course of its oxidation and, for this reason, the oscillating system is homogeneous and closed unless an emulsion of the bromo derivative appears. The basic characteristics of the BZ reaction with the ethyl ester of 3-oxobutanoic acid was described by *Zhabotinskii* [1, 2], *Heilweil et al.* [3], and *Winfree* [4]. In relation to this reaction we described the kinetics of oxidation of ethyl ester of 3-oxobutanoic acid by the Ce(IV) ions [5] and the behaviour of the BZ system in the presence of the Ce(III)—Ce(IV) [6] as well as Mn(II)—Mn(III) redox catalyst [7]. Two types of oscillations, "high-frequency" and "low-frequency", in the system H_2SO_4—$NaBrO_3$—ethyl ester of 3-oxobutanoic acid—(Ce(III)—Ce(IV)) or (Mn(II)—Mn(III)) have been described by *Salter et al.* [8]. The dual-frequency oscillations in the Belousov—Zhabotinskii reaction system with the methyl ester of 3-oxobutanoic acid have been found by *Tsukada* [9] recently. The reaction system of the Belousov—Zhabotinskii type with the ethyl ester of 3-oxobutanoic acid in the presence of ferroin-ferriin redox catalyst exhibits an oxygen-induced excitability [10, 11]. Recently, we have reported a spectrophotometric study of bromate-driven oscillations of the Belousov—Zhabotinskii type with the ethyl ester of 3-oxobutanoic acid as substrate and the redox catalyst either Ce(III)—Ce(IV) or Mn(II)—Mn(III) in the presence of Ag^+ ions [12].

The aim of this work is to investigate the kinetics of oxidation of a series of 3-oxobutanoic esters by the Ce(IV) ions and the oscillatory behaviour of reaction systems of Belousov—Zhabotinskii type with corresponding members of the same series of esters, in order to find the correlation between the parameters of BZ reaction and Taft substituent constants.

Experimental

The kinetics of oxidation of 3-oxobutanoic acid esters by cerium(IV) sulfate in a solution of sulfuric acid was investigated spectrophotometrically on the basis of the time dependence of absorption of the Ce(IV) ions at the wavelength of $\lambda_{max} = 320$ nm. The spectrophotometric measurements were performed by the use of a spectrophotometer Specord UV VIS (Zeiss, Jena) which was equipped with a temperature-controlling block joined to an ultrathermostat U 10 (Medingen, GDR). The value of rate constant was measured within the accuracy of ± 4 %. The values given in the table and in the figure are means of four independent measurements. The procedure of polarographic, potentiometric, and spectrophotometric investigation of the course of the BZ reaction was described in papers [5—7] and [10—12].

The methyl ester, ethyl ester, and isopropyl ester of 3-oxobutanoic acid (Lonza, Switzerland) were anal. grade chemicals, the butyl ester and propyl ester of 3-oxobutanoic acid were synthesized according to [13]. All other chemicals and solvents used for the preparation of solutions were anal. grade.

Results and discussion

The kinetics of oxidation of methyl, ethyl, propyl, isopropyl, and butyl esters of 3-oxobutanoic acid by cerium(IV) sulfate in 1 M solution of sulfuric acid was

Table 1

Values of the rate constant k_2 in relation to σ^* constants
3.3×10^{-4} M-$Ce(SO_4)_2$, 1.5×10^{-2} M ester of 3-oxobutanoic acid, 1 M-H_2SO_4, temperature of 20 °C

Ester of 3-oxobutanoic acid	Taft σ^* constant	$k_2/(dm^3\,mol^{-1}\,s^{-1})$
Methyl	0	9.40
Ethyl	−0.10	8.10
Propyl	−0.125	7.81
Isopropyl	−0.19	6.60
Butyl	−0.13	7.76

studied at the temperature of 20 °C. The partial reaction orders of both reactants have been determined to be one and the resulting rate equation is as follows: $-\,d[Ce(IV)]/dt = k_2[Ce(IV)]\,[ester]$. The second-order rate constant k_2 for Ce(IV) oxidation of esters of 3-oxobutanoic acid in the solution of 1 M-H_2SO_4 can be correlated with the Taft substituent σ^* constants (Table 1). Using the values of the second-order constants k_2 for methyl, ethyl, propyl, isopropyl, and butyl ester of 3-oxobutanoic acid, a linear plot was obtained between $\log k_2$ and σ^* which gave the value of ϱ^* constant equal to 0.78 (Fig. 1).

The same series of esters was used for the kinetic study of the Belousov—Zhabotinskii reaction. The course of BZ reaction was followed in the presence of single esters of 3-oxobutanoic acid (Fig. 2). It was evaluated as the time

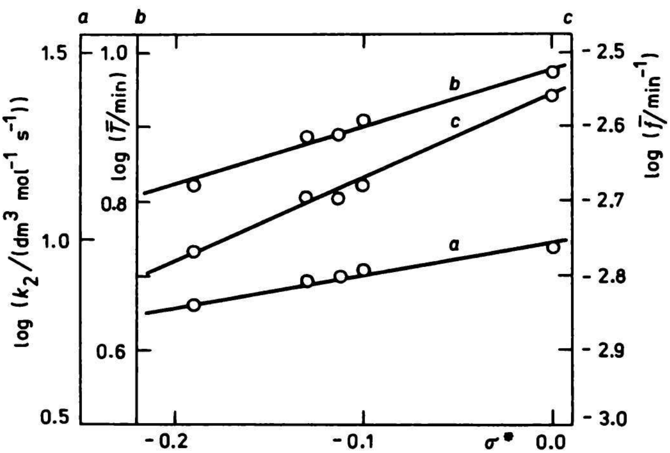

Fig. 1. Correlations of the rate constant k_2 and of BZ reaction parameters with σ^* constants. 3.3×10^{-4} M-$Ce(SO_4)_2$, 1.5×10^{-2} M ester of 3-oxobutanoic acid, 1 M-H_2SO_4, temperature of 20 °C. The initial concentrations of reactants during the BZ reaction are the same as in Fig. 2.

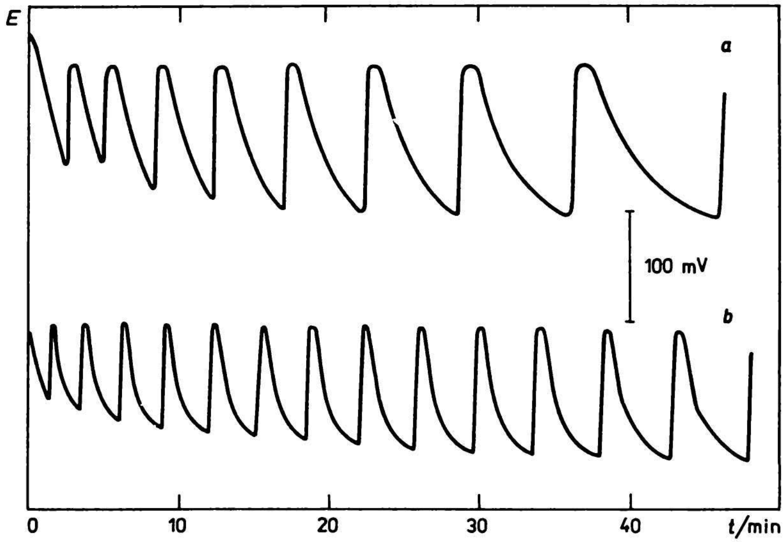

Fig. 2. Influence of the nature of ester on the course of the BZ reaction. 8×10^{-4} M-$Ce(SO_4)_2$, 1.5×10^{-2} M-$NaBrO_3$, 1 M-H_2SO_4. *a*) 0.006 M isopropyl ester, *b*) 0.006 M methyl ester, temperature of 20 °C.

dependence of the period of oscillations or in their subsequently following order (Fig. 3). On the basis of these dependences the values of the averaged period of oscillations and of the averaged frequency of oscillations were evaluated. Using these values for the mentioned series of esters, a linear plot was obtained

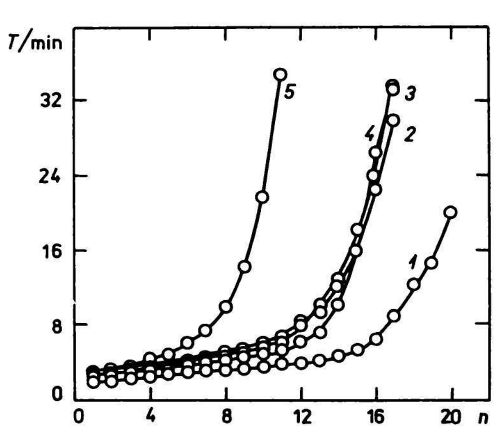

Fig. 3. The period of oscillations during the BZ reaction in the subsequently following order *n*. The initial concentrations as in Fig. 2.
1. Methyl ester; *2.* propyl ester; *3.* ethyl ester; *4.* butyl ester; *5.* isopropyl ester; temperature of 20 °C.

between log $\bar{T}$ or log $\bar{f}$ and σ^* which gave ϱ^* value of 0.79 or 1.11, correspondingly (Fig. 1).

The Field—Körös—Noyes (FKN) mechanism of the Belousov—Zhabotinskii reaction can be summarized in three main processes: process *A* , process *B*, and process *C*. The details of these processes are described for example in our book [14]. Process *C* corresponds to the reduction of Ce(IV) ions by a substrate. From the results presented we can conclude that the nature of a substituent influences not only the reactivity between the Ce(IV) ions and ester as a substrate, but also through the process *C* it quantitatively influences the main parameters of the BZ reaction.

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