Kinetics of the oxidation of ethyl ester of 3-oxobutyric acid by the cerium(IV) ions in relation to the Belousov—Zhabotinskii reaction

Ľ. TREINDL and P. KAPLÁN

Department of Physical Chemistry, Faculty of Natural Sciences,
Komenský University, 816 50 Bratislava

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The oxidation of ethyl ester of 3-oxobutyric acid by the Ce(IV) ions in the solution of sulfuric acid is an inner-sphere reaction, which proceeds through an intermediary complex. This reaction is a first-order reaction with respect to both reactants and is catalyzed by the H_3O^+ ions. Its rate is inversely proportional to concentration of the HSO_4^- ions as well as of the Ce(III) ions. A plausible reaction mechanism has been proposed and the rate equation derived on the basis of this mechanism is in good agreement with the experimental equation. The activation parameters $\Delta H^{\neq} = 51.6\ \text{kJ mol}^{-1}$ and $\Delta S^{\neq} = -53\ \text{J K}^{-1}\ \text{mol}^{-1}$ have been evaluated from the temperature dependence of the rate constant.

The modified Belousov—Zhabotinskii reaction system containing ethyl ester of 3-oxobutyric acid as substrate is noteworthy by the fact that regular oscillations of the concentration of the Ce(IV) ions arise in an undisturbed system without any induction period even if the electrolyte is not stirred. The course of oscillations was investigated polarographically and spectrophotometrically and the corresponding activation parameters were evaluated on the basis of their dependence on temperature.

Окисление этилового эфира 3-оксобутановой кислоты ионами Ce(IV) в растворе серной кислоты является внутрисферной реакцией, которая протекает через образование промежуточного комплекса. Реакция первого порядка по отношению к обоим реактантам катализируемая ионами H_3O^+ и ее скорость обратно пропорциональна концентрации ионов HSO_4^- и Ce(III). Был предложен вероятный механизм реакции и уравнение скорости реакции, полученное на его основании, хорошо согласуется с экспериментом. Из температурной зависимости константы скорости были получены параметры активации, $\Delta H^{\neq} = 51{,}6$ кДж моль$^{-1}$ и $\Delta S^{\neq} = -53$ Дж K^{-1} моль$^{-1}$.

Модификация реакционной системы Белоусова—Жаботинского с этиловым эфиром 3-оксобутановой кислоты в качестве субстрата интересна тем, что регулярные колебания концентрации ионов Ce(IV) появляются без индукционного периода даже в системе без перемешивания электролита. За ходом осцилляций наблюдали полярографически и спектрофотометрически и по их температурной зависимости были найдены соответствующие параметры активации.

We synoptically reviewed oscillation reactions earlier [1]. The kinetics and mechanism of the Belousov—Zhabotinskii reaction were studied by using the virtue of rotating platinum electrode [2]. The influence of some electrolytes [3] and oxygen [4] on the fundamental kinetic parameters of this reaction was also described. Recently, we described the behaviour of the Belousov—Zhabotinskii oscillation system containing 2,4-pentadione as substrate [4, 5].

The modified Belousov—Zhabotinskii reaction in the presence of ethyl ester of 3-oxobutyric acid functioning as substrate was described by *Zhabotinskii* [6] and *Winfree* [7]. The kinetics of the oxidation of this substrate by the Ce(IV) ions was studied by *Panigrahi* and *Misro* [8] who, however, presented only elementary kinetic data of this reaction in the scope of complex investigations of keto compounds. More detailed kinetic data concerning this system are lacking for the time being and, for this reason, its kinetic study is the topic of the present paper.

Experimental

The kinetics of the oxidation of ethyl ester of 3-oxobutyric acid by the Ce(IV) ions was studied polarographically by recording the dependence of limiting diffusion current of the Ce(IV) ions on time using a rotating platinum electrode at the potential $E = -0.05$ V against the potential of a Hg_2SO_4 electrode in a 2 M solution of H_2SO_4. The experimental installation was described in paper [2].

A spectrophotometer Specord UV VIS (Zeiss, Jena) was used for spectrophotometric measurements. The measurements were carried out in 10 mm cells placed in a temperature-controlled block joint to a thermostat. The course of reactions was observed by means of the temporal change in absorbance at $\lambda_{max} = 320$ nm. The presented values of rate constants were calculated as an average of four independent measurements.

The chemicals used were anal. grade reagents and redistilled water was used for preparation of the solutions.

Results

Kinetics of the oxidation of ethyl ester of 3-oxobutyric acid by the Ce(IV) ions

It has been evidenced by the integral method that the oxidation of ethyl ester of 3-oxobutyric acid by the Ce(IV) ions is a reaction of the first order with respect to the

Ce(IV) ions as well as to substrate. The dependence of limiting diffusion current of the Ce(IV) ions on time corresponds to kinetic equation of the first order in the interval of the first two half-times of the reaction. The experimental rate constant (s^{-1}) is a linear function of concentration of the substrate within the concentration range 3×10^{-3}—3×10^{-2} M (Fig. 1). The slope of this graphical relation passing through the origin of coordinate system gives the value of rate constant of the second-order reaction $k = 7.3\ s^{-1}\ mol^{-1}\ dm^3$ at 20°C. The activation parameters, *i.e.* activation enthalpy $\Delta H^{\neq} = 51.6\ kJ\ mol^{-1}$ and activation entropy $\Delta S^{\neq} = -53\ J\ K^{-1}\ mol^{-1}$ were evaluated by the method of least squares from the temperature dependence of rate constant in the temperature interval 10—35°C on the basis of the Eyring equation.

The experimental rate constant linearly increases with concentration of the H_3O^+ ions and the corresponding graph passes through the origin of coordinate system. The slope of this graph gives the value of catalytic constant $k_{H^+} = 1.0 \times 10^{-2}\ s^{-1}\ mol^{-1}\ dm^3$. The value of rate constant decreases with increasing value of ionic strength (Fig. 2). The plot of log k against $\sqrt{I}/(1+\sqrt{I})$ is linear, the slope being -1.5. The rate constant also decreases with increasing concentration of the HSO_4^- ions (Table 1). The dependence of the rate constant on the inverse value of concentration of the hydrogen sulfate ions is linear. On addition of the Ce(III) ions into the solution, the value of rate constant decreases (Table 2). The dependence of the rate constant on the inverse value of concentration of the Ce(III) ions is linear. The course of polarometric titration of the Ce(IV) ions with the solution of substrate indicates consumption of two Ce(IV) ions for a molecule of ethyl ester of 3-oxobutyric acid.

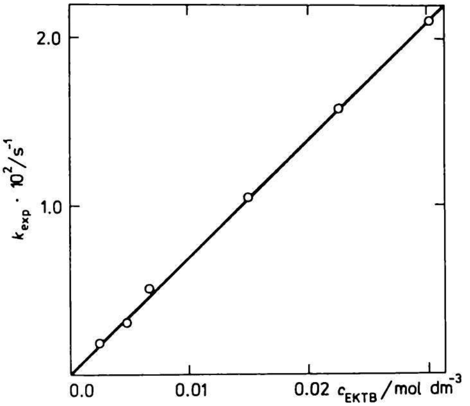

Fig. 1. Variation of experimental rate constant with concentration of ethyl ester of 3-oxobutyric acid (EKTB). 3.3×10^{-4} M-$Ce(SO_4)_2$, 1 M-H_2SO_4, 20°C.

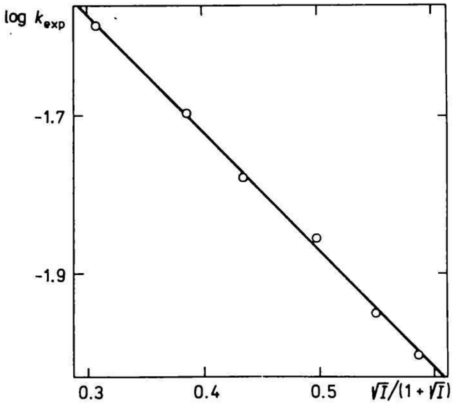

Fig. 2. Variation of experimental rate constant with ionic strength. 3.3×10^{-4} M-$Ce(SO_4)_2$, 4.0×10^{-3} M-EKTB, 0.2 M-H_2SO_4, 20°C.

Table 1

Variation of experimental rate constant with concentration of the HSO_4^- ions
3.3×10^{-4} M-$Ce(SO_4)_2$, 4×10^{-3} M-$CH_3COCH_2COOC_2H_5$, 2 M-H_3O^+, 20°C

$c_{HSO_4^-}$/mol dm^{-3}	$k_{exp}\cdot10^2$/s^{-1}
0.25	3.5
0.50	2.8
0.75	2.5
1.00	2.3
1.50	2.1
2.00	2.0

Table 2

Variation of experimental rate constant with
concentration of the Ce(III) ions
3.3×10^{-4} M-$Ce(SO_4)_2$, 4.7×10^{-3} M-$CH_3COCH_2COOC_2H_5$, 1 M-H_2SO_4, 20°C

$c_{Ce_2(SO_4)_3}$/mol dm^{-3}	$k_{exp}\cdot10^2$/s^{-1}
—	3.1
3.3×10^{-4}	2.2
6.6×10^{-4}	1.7
9.9×10^{-4}	1.4
2.0×10^{-3}	0.8

The Belousov—Zhabotinskii reaction involving ethyl ester of 3-oxobutyric acid as substrate

The modified Belousov—Zhabotinskii oscillation system comprising 2×10^{-3} M-$Ce(SO_4)_2$, 6×10^{-2} M-$KBrO_3$, and 2×10^{-2} M-$CH_3COCH_2COOC_2H_5$ in 1 M-H_2SO_4 exhibits regular oscillations of concentration of the Ce(IV) ions without any induction period. In contrast to the Belousov—Zhabotinskii system containing malonic acid as substrate the described system oscillates even without any stirring of the electrolyte. The course of oscillations may be reproducibly investigated by polarography with a rotating platinum electrode. The characteristic parameters of oscillations do not change with potential of the indication electrode (Table 3).

The corresponding thermodynamic activation quantities [2—5] (Table 4, Fig. 3) were evaluated on the basis of the temperature dependence of the logarithm of period of the first oscillation, logarithm of the time of existence of oscillations, and logarithm of the frequency of oscillations by means of the Arrhenius equation. The linear course of these relationships was to be obtained only if the solution was previously thoroughly bubbled with nitrogen used in electric bulb industry.

Table 3

Characteristic parameters of oscillations at varying potential of the indication electrode

2×10^{-3} M-$Ce(SO_4)_2$, 2×10^{-2} M-EKTB, 6×10^{-2} M-$KBrO_3$, 1 M-H_2SO_4

E/V	First period of oscillations s	Period of time of oscillations s	Frequency of oscillations s^{-1}
−0.05	49	1674	1.14×10^{-2}
+0.10	49	1698	1.12×10^{-2}
+0.25	49	1602	1.19×10^{-2}
+0.50	49	1800	1.06×10^{-2}

Table 4

Activation parameters determined from temperature dependence of the corresponding parameters of oscillations

Experimental conditions as in Table 3

Determination from temperature dependence	E/kJ mol^{-1}	A/s^{-1}
Period of the first oscillation	49.3	8.56×10^{6}
Period of time of oscillations	65.7	1.97×10^{8}
Frequency	52.0	1.43×10^{7}

The oscillations of concentration of the redox catalyst could be also investigated spectrophotometrically (Fig. 4) by recording the dependence of absorbance of the Ce(IV) ions on time at $\lambda_{max}=320$ nm. At higher temperatures (35°C), the simple regular oscillations turn into complicated "doubled" oscillations resembling modulation of a carrier wave (Fig. 5).

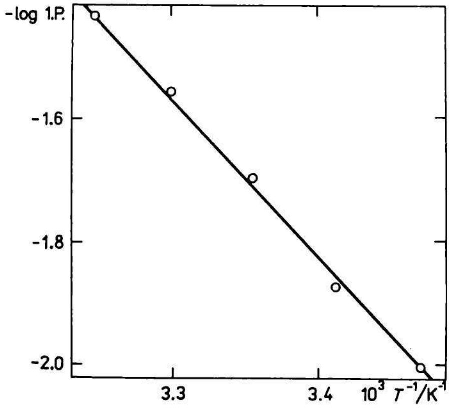

Fig. 3. Temperature dependence of the first period of oscillations.
Experimental conditions as in Table 3.

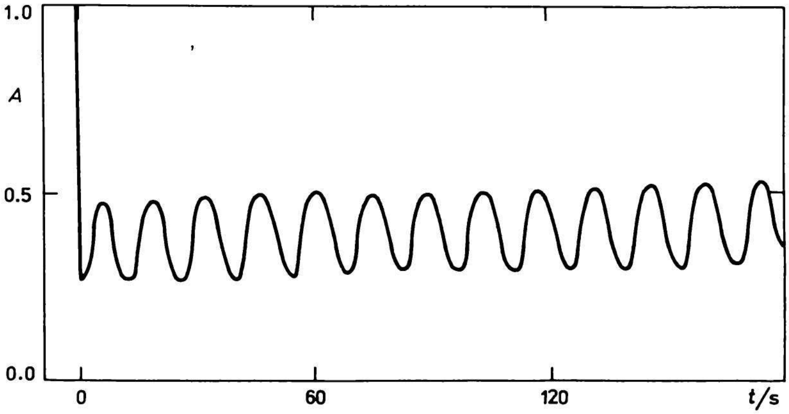

Fig. 4. Oscillations of absorbance at $\lambda_{\max}=320$ nm.
4×10^{-4} M-$Ce(SO_4)_2$, 6×10^{-2} M-$KBrO_3$, 4×10^{-2} M-EKTB, 1 M-H_2SO_4, 30°C.

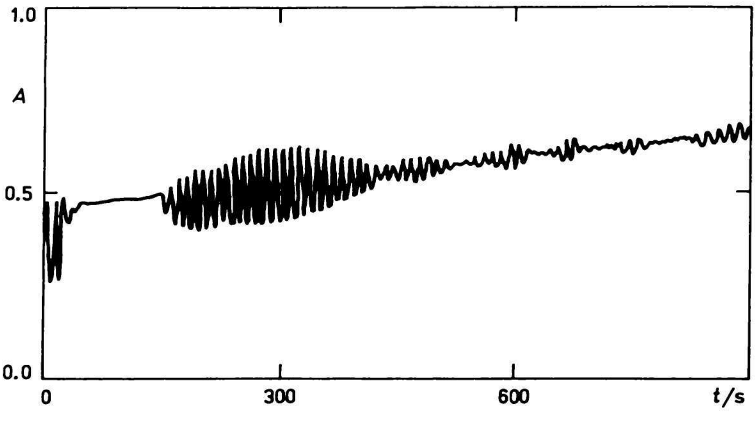

Fig. 5. Double oscillations.
Experimental conditions as in Fig. 4, 35°C.

Discussion

On the basis of the described results, the rate equation of the oxidation of ethyl ester of 3-oxobutyric acid by the Ce(IV) ions in a sulfuric acid solution may be written as follows

$$-\frac{d[\mathrm{Ce(IV)}]}{dt}=\frac{k[\mathrm{Ce(IV)}]\,[\mathrm{CH_3COCH_2COOC_2H_5}]\,[\mathrm{H_3O^+}]}{[\mathrm{Ce(III)}]\,[\mathrm{HSO_4^-}]} \qquad (1)$$

This rate equation can be also theoretically derived if we assume the reaction mechanism according to which the enol form of ethyl ester of 3-oxobutyric acid is attacked by the species $Ce(SO_4)_2$ to give the intermediary complex

$$Ce(SO_4)_2 + \text{enol} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce(SO_4)_2 - \text{enol} \tag{A}$$

According to *Hardwick* and *Robertson* [9], the following mobile equilibria of the Ce(IV) ions manifest themselves in a solution of sulfuric acid

$$Ce^{4+} + HSO_4^- \overset{K_1'}{\rightleftharpoons} CeSO_4^{2+} + H^+ \tag{B}$$

$$CeSO_4^{2+} + HSO_4^- \overset{K_2'}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \tag{C}$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3'}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+ \tag{D}$$

In the subsequent step which is slow and rate-determining the intermediary complex decays because of the intramolecular redox reaction

$$Ce(SO_4)_2 - \text{enol} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R\bullet + Ce(SO_4)_2^- \tag{E}$$

and the formed intermediary radical is rapidly oxidized in the following step

$$R\bullet + Ce(SO_4)_3^{2-} \overset{k_4}{\rightarrow} P + Ce(SO_4)_2^- \tag{F}$$

The sum of particular steps gives the stoichiometric equation the coefficients of which were verified by polarometric titration.

On the basis of the values of consecutive complexity constants [9] $K_1' = k_1'/k_{-1}' = 3500$, $K_2' = k_2'/k_{-2}' = 200$, and $K_3' = k_3'/k_{-3}' = 20$, we may assume for 1 M sulfuric acid solution that the analytical concentration of the Ce(IV) ions $[Ce(IV)] \approx [Ce(SO_4)_3^{2-}]$ [4] and thus it is valid according to the proposed reaction scheme

$$-\frac{d[Ce(SO_4)_3^{2-}]}{dt} = k_{-3}'[Ce(SO_4)_3^{2-}]\,[H^+] - k_3'[Ce(SO_4)_2]\,[HSO_4^-] + \\ + k_4[Ce(SO_4)_3^{2-}]\,[R\bullet] \tag{2}$$

In a stationary state it holds

$$\frac{d[R\bullet]}{dt} = k_3[Ce(SO_4)_2 - \text{enol}] - k_{-3}[R\bullet]\,[Ce(SO_4)_2^-] - \\ - k_4[R\bullet]\,[Ce(SO_4)_3^{2-}] = 0 \tag{3}$$

By solving these equations, we obtain

$$-\frac{\mathrm{d}[\mathrm{Ce(SO_4)_3^{2-}}]}{\mathrm{d}t}=\frac{k_3k_4K_1[\mathrm{Ce(SO_4)_3^{2-}}]^2[\mathrm{H^+}]\,[\mathrm{enol}]}{K_3'[\mathrm{HSO_4^-}]\,(k_{-3}[\mathrm{Ce(SO_4)_2^-}]+k_4[\mathrm{Ce(SO_4)_3^{2-}}])} \tag{4}$$

At a low concentration of the Ce(III) ions in solution the reverse step of reaction (*E*) is much slower than the oxidation of the free radical, *i.e.*

$$k_{-3}[\mathrm{Ce(SO_4)_2^-}]\ll k_4[\mathrm{Ce(SO_4)_3^{2-}}] \tag{5}$$

and we may write

$$-\frac{\mathrm{d}[\mathrm{Ce(SO_4)_3^{2-}}]}{\mathrm{d}t}=\frac{k_3K_1[\mathrm{Ce(SO_4)_3^{2-}}]\,[\mathrm{enol}]\,[\mathrm{H^+}]}{K_3'[\mathrm{HSO_4^-}]} \tag{6}$$

Theoretical rate eqn (*6*) is practically consistent with experimental rate eqn (*1*) provided the concentration of the Ce(III) ions remains constant in the course of reaction.

As we have already stated, the modified Belousov—Zhabotinskii reaction system containing ethyl ester of 3-oxobutyric acid is noteworthy by the fact that it exhibits oscillations of the concentration of the Ce(IV) ions without any induction period and even in undisturbed state when the electrolyte is not stirred. The reaction courses investigated spectrophotometrically are in good agreement with polarographic results obtained by means of a rotating platinum electrode. These facts suggest that a "homogeneous oscillation system" exists in this case. This system might be mechanistically and mathematically analyzed more easily than the Belousov—Zhabotinskii system containing malonic acid. Its merit may also consist in the fact that the oscillations start immediately after mixing the components of the system without any induction period.

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