KINETICS OF OXIDATION OF α-KETOGLUTARIC ACID WITH Ce(IV) IONS IN RELATION TO BELOUSOV-ZHABOTINSKII REACTION

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Oxidation of α-ketoglutaric acid with Ce(IV) ions in a solution of sulphuric acid is a reaction of the first order with respect to both Ce(IV) ions and substrate, is acid catalysed, and its rate is proportional to the reciprocal square of the equilibrium HSO_4^- concentration. From the temperature dependence of the rate constant in 1·5M-H_2SO_4, the activation parameters were determined as $\Delta H^{\neq} = 57$ kJ/mol and $\Delta S^{\neq} = -45$ J mol^{-1} K^{-1}. The redox reaction proper consists apparently of two steps: in the first one, the enol form of α-ketoglutaric acid reacts with Ce(IV) ions with the formation of the corresponding radical; in the second one, the latter is oxidised further with Ce(IV) to give malonic and succinic acids. Conditions are indicated under which α-ketoglutaric acid serves as substrate for the Belousov–Zhabotinskii oscillation reaction in the presence of Ce(IV)–Ce(III) redox catalyst. Oscillations of Ce(IV) and Br_2 concentrations, shifted in phase, can be recorded polarographically with a rotating platinum electrode.

Since α-ketoglutaric acid is important for biochemical processes in organic cells, it has been studied in connexion with transamination reactions, transport in mitochondria, enzymatic reactions, succinate-glycine cycle, aerobic deamination, *etc.* Its oxidation with metal ions has been studied relatively little[1]. Since it can also form the substrate for the Belousov–Zhabotinskii reaction, we decided to study its oxidation with Ce(IV) ions.

EXPERIMENTAL

The reaction between $Ce(SO_4)_2$ and α-ketoglutaric acid in a solution of sulphuric acid was studied polarographically. The limiting diffusion current of Ce(IV) ions on a rotating Pt electrode at 0 V ($Hg/HgSO_4$) in 2M-H_2SO_4 was recorded. The frequency of revolution was 20 s^{-1}. The solution was placed in a Kalousek cell with a thermostated mantle piece and was tempered 10–15 min prior to the measurement while bubbling with pure nitrogen. Oscillations of Ce(IV) and Br_2 concentrations were followed in the same experimental setup. The chemicals used were of reagent grade.

RESULTS

The oxidation of α-ketoglutaric acid with Ce(IV) ions in a solution of sulphuric acid is a reaction of the first order with respect to the concentration of Ce(IV) ions. The dependence of the logarithm of the diffusion current of Ce(IV) ions on the time is linear in the interval of the first two reaction half-times. The rate constant, determined from the slope of this dependence, is a linear function of the substrate concentration from $3{\cdot}3 \,.\, 10^{-4}$ to 10^{-2} mol/l (Fig. 1). The slope of this dependence gives the rate constant k_{II}. In this way, the partial reaction order with respect to α-ketoglutaric acid was determined as 1 at various temperatures. From the temperature dependence of k_{II} and the Eyring equation, the activation parameters were determined by the least squares method as $\Delta H^{\neq} = 57$ kJ/mol and $\Delta S^{\neq} = -45 \text{ J mol}^{-1} \,.\, \text{K}^{-1}$ (Fig. 2).

The studied reaction is acid catalysed; the dependence of the experimental rate constant on the concentration of H_3O^+ ions at constant ionic strength (2·2 mol/dm³), concentration of HSO_4^- ions and temperature (25°C) is linear according to the equation $k_{\mathrm{exp}} = k_0 + k_{\mathrm{H}^+}[H_3O^+]$, where $k_0 = 8{\cdot}2 \,.\, 10^{-3} \text{ s}^{-1}$ and $k_{\mathrm{H}^+} = 5{\cdot}9 \,.\, 10^{-3} \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$.

The dependence of the logarithm of the experimental rate constant on the ionic strength is linear in the interval $I = 1{\cdot}5 - 2{\cdot}4$ mol/dm³ at constant concentration

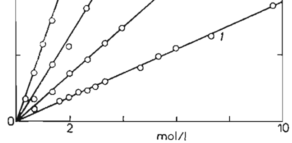


FIG. 1

Dependence of experimental rate constant on concentration of α-ketoglutaric acid. 1·5 mol/l H_2SO_4, 6·6 . 10^{-4} mol/l $Ce(SO_4)_2$. *1* 17·1°C; *2* 26°C; *3* 32·5°C; *4* 40°C

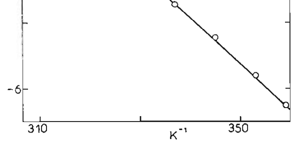


FIG. 2

Temperature dependence of second-order rate constant. 1·5 mol/l H_2SO_4, 5·5 . 10^{-4}lmol/l $Ce(SO_4)_2$, 2·8 . 10^{-3} mol/l α-ketogutaric acid of H_3O^+ and HSO_4^- ions and at 25°C (Table I). The value of k_{cxp} decreases with increasing concentration of HSO_4^- ions at constant ionic strength and pH (Fig. 3); a linear dependence is obtained by plotting k_{cxp} against $1/[HSO_4^-]^2$.

Polarometric titration of the limiting diffusion current of Ce(IV) ions with α-ketoglutaric acid revealed that two Ce(IV) ions react with one molecule of the acid.

Suitable substrates for the Belousov–Zhabotinskii reaction are compounds containing a hydrogen atom which is easily replaced by bromine and is located close to a carboxyl group. Such compounds are, according to Franck[2] and Cooke[3], malonic, bromomalonic, citric, malic, maleic, 3,4,5-trioxybenzoic, acetoacetic, oxalacetic, acetonedicarboxylic, and barbituric acids, further ethyl aceto acetate, acetone, 2,4--pentanedione, 2,5-hexanedione, and their fluoro derivatives. Since α-ketogluaric acid is similar to acetonedicarboxylic (β-ketoglutaric) acid, it could also be expected to be a suitable substrate.

The oscillation character of the Belousov–Zhabotinskii system with this acid depends on the concentrations of the reaction components and on the duration

TABLE I

Influence of ionic strength on the rate constant. 1·5 mol/l H_2SO_4, 2·7 . 10^{-3} mol/l α-ketoglutaric acid, 5 . 10^{-4} mol l $Ce(SO_4)_2$, 25°C

I, mol/l	1·5	1·68	1·85	2·03	2·2	2·39
$k_{exp} . 10^3$	7·95	6·2	4·8	3·4	3·5	2·4

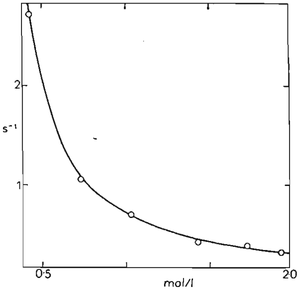


FIG. 3

Dependence of experimental rate constant on concentration of HSO_4^- ions. 2·5 . 10^{-4} mol/l $Ce(SO_4)_2$, 5 . 10^{-4} mol/l α-ketoglutaric acid, 0·22 mol/l H_2SO_4; 25°C of the bromination reaction prior to adding the cerium catalyst. Oscillations of the diffusion currents of Ce(IV) ions and bromine were observed on a rotating platinum electrode during bubbling with pure nitrogen a solution of $1{\cdot}25 . 10^{-4}\text{M}$ $Ce(SO_4)_2$, $0{\cdot}011\text{M}$-$NaBrO_3$, $0{\cdot}082\text{M}$ α-ketoglutaric acid, and $1{\cdot}5\text{M}$-H_2SO_4 at 40°C (Fig. 4). The oscillations with a sharp peak correspond to Ce(IV) ions and those with a blunt peak, shifted in phase, to bromine. Indeed, the amplitude of the former increased by adding $Ce(SO_4)_2$ and that of the latter was influenced by bubbling nitrogen (the bromine carried away with nitrogen was proved by the reaction with fluoresceine). If both the rotating Pt electrode and bubbling with nitrogen are stopped, the oscillations become irregular.

The character and parameters of the oscillations depend on the duration of the reaction between BrO_3^- ions and the substrate prior to addition of the cerium catalyst (Table II). The temperature dependences of the induction period, period of the first oscillation, duration of the oscillations, and their frequency obey the Arrhenius equation, whence the respective activation energies were evaluated as: $E_{\text{i.p.}} = 28$ kJ/mol, $E_{\text{T},1} = 23$ kJ/mol, $E_{\text{T}} = 33$ kJ/mol, and $E_{\text{f}} = 26$ kJ/mol.

DISCUSSION

Based on the mentioned results, the rate equation can be written as

$$-\frac{\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = (k_0 + k_{\mathrm{H}^+}[\mathrm{H_3O^+}])\,[\mathrm{Ce(IV)}]\,[\mathrm{substrate}]\,, \qquad (1)$$

where the first multiplier represents the second-order rate constant (found experimentally). Its temperature dependence gives $\Delta H^{+} = 57$ kJ/mol and $\Delta S^{+} = -45$ J . . mol^{-1} K^{-1}, which involve activation parameters corresponding both to k_0 and

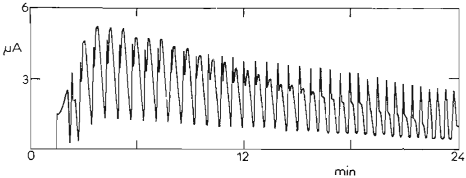
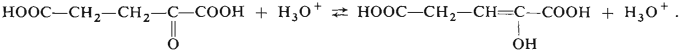


FIG. 4

Polarographic record of Belousov–Zhabotinskii reaction with α-ketoglutaric acid. 1·5 mol/l H_2SO_4, $1{\cdot}25 . 10^{-4}$ mol/l $Ce(SO_4)_2$, 0·125 mol/l α-ketoglutaric acid, $1{\cdot}12 . 10^{-2}$ mol/l $NaBrO_3$; 40°C, $E_p = 0$ V against $Hg/HgSO_4$

the catalytic constant k_{H^+}. The latter is probably related to a specific acid catalysis of enolization of the substrate according to



$$HOOC-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-COOH + H_3O^+ \rightleftarrows HOOC-CH_2-CH=\underset{\underset{OH}{|}}{C}-COOH + H_3O^+ . \qquad (A)$$

The redox reaction proper consists probably of two steps. In the first one, Ce(IV) ion react with the enol form of the acid with the formation of the corresponding radical. In the second one, the latter is oxidised further with Ce(IV) ions to give malonic and oxalic acids. The influence of ionic strength on the reaction rate is not in accord with the equation of Bjerrum and Brönsted for the primary salt effect, since the logarithm of k_{cxp} is a linear function of the ionic strength. This can be expected for a reaction of a neutral molecule with an ion in concentrated solutions, where according to Hückel

$$-\log f_i = \frac{Az_i^2 \sqrt{I}}{1 + B\sqrt{I}} + CI , \quad -\log f_M = CI . \qquad (2), (3)$$

(Eq. (2) holds for an ion, (3) for a molecule.) It can be assumed that the activity coefficient of the activated complex is given by an equation similar to (2). From the equation describing the primary salt effect

$$\log k_{cxp} = \log k_0 + \log (f/f_i f_M) \qquad (4)$$

we obtain

$$\log (k_{cxp}/k_0) = CI . \qquad (5)$$

TABLE II

Dependence of parameters for Belousov–Zhabotinskii reaction on duration of reaction between BrO_3^- ions and α-ketoglutaric acid at 30°C

Time min	Number of osc.	Duration of osc.	Period of 1st osc., min	Mean freq. min^{-1}
0	89	93	1·2	0·956
20	93	131	1·8	0·709
40	102	120	1·5	0·850
130	85	73	0·85	1·164
225	28	21	0·80	1·333

The decrease of the rate constant with increasing concentration of HSO_4^- ions can be attributed to a shift in the equilibrium of Ce(IV) sulphate complexes in favour of the less reactive complexes with more coordinated SO_4^{2-} ions. According to Hardwick and Robertson[4] the following equilibria should be considered:

$$Ce^{4+} + HSO_4^- = CeSO_4^{2+} + H^+ , \qquad (B)$$

$$CeSO_4^{2+} + HSO_4^- = Ce(SO_4)_2 + H^+ , \qquad (C)$$

$$Ce(SO_4)_2 + HSO_4^- = Ce(SO_4)_3^{2-} + H^+ . \qquad (D)$$

At high concentration of the acid, the equilibrium (*B*) may be neglected, the concentration of Ce^{4+} ions being negligible. The equilibrium concentration of $CeSO_4^{2-}$ ions can be expressed as

$$[CeSO_4^{2+}] = [Ce(SO_4)_3^{2-}]\,[H^+]^2/K_2K_3[HSO_4^-]^2 \qquad (6)$$

and from the rate equation $v = k[\text{enol}][CeSO_4^{2+}]$ we obtain

$$v = k[\text{enol}]\,[Ce(SO_4)_3^{2-}][H^+]^2/K_2K_3[HSO_4^-]^2 . \qquad (7)$$

In 1·5M-H_2SO_4, we have the total cerium in the form of $Ce(SO_4)_3^{2-}$ and

$$k_{\text{exp}} = k[\text{enol}][H^+]^2/K_2K_3[HSO_4^-]^2 . \qquad (8)$$

This dependence of k_{exp} on the concentration of HSO_4^- ions was proved experimentally (Fig. 3), hence $CeSO_4^{2-}$ ions are the reactive component.

The oscillations of Ce(IV) ions and bromine, which are shifted in phase[7], can be followed at the same time by means of a rotating platinum electrode at 0 V against 2M-Hg_2SO_4 electrode (Fig. 4). It is remarkable that the temperature dependences of the induction period, period of the first oscillation, duration of the oscillations, and their frequency obey the Arrhenius equation. The corresponding activation energies serve as quantitative characteristics of the chemical oscillator under study. Its main parameters depend on the time of bromation of the substrate. Similarly to other studies[5,6], also here it is necessary to consider the following main steps

$$BrO_3^- + Br^- + 2\,H^+ \rightarrow HBrO_2 + HOBr , \qquad (E)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2\,HOBr , \qquad (F)$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O , \qquad (G)$$

followed by the bromination of the substrate, whose rate-determining step is probably enolization. The oscillating increase of the bromine concentration obviously corresponds to the time intervals in which a sufficient quantity of the accumulated enol form of α-ketoglutaric acid is lacking.

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