KINETICS OF OXIDATION OF 2,4-PENTANEDIONE WITH Ce(IV) IONS IN RELATION TO BELOUSOV-ZHABOTINSKII REACTION

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Received July 10th, 1980

Oxidation of 2,4-pentanedione with Ce(IV) ions in a solution of sulphuric acid is an inner-sphere reaction which proceeds *via* an intermediary complex. The reaction is of the first order with respect to both reactants, it is catalysed with H_3O^+ ions, and its rate diminishes with increasing concentrations of HSO_4^- and Ce(III) ions. According to the proposed mechanism, the rate-determining reaction step is an intramolecular redox step of the intermediary complex. The modified Belousov–Zhabotinskii reaction with 2,4-pentanedione as substrate is interesting in that oscillations with an increasing amplitude are formed after an induction period even in the absence of stirring.

Oscillation reactions were already reviewed by us[1]. The kinetics and mechanism of the Belousov–Zhabotinskii (B.–Zh.) reaction were investigated with the use of a rotating platinum electrode[2] and the influence of some electrolytes[3] and oxygen[4] on the basic kinetic parameters was described.

The modified B.–Zh. reaction with 2,4-pentanedione as substrate was studied by several authors. Bowers and coworkers[5] pointed out that this reaction is not accompanied with evolution of gaseous products and can be hence carried out in a closed system. Janjic and coworkers[6] followed potentiometrically the oscillations in the concentrations of Br^-, Ce^{3+}, Ce^{4+} and Ce^{+4} ions in the system of Ce(IV), $KBrO_3$ and 2,4-pentanedione. They measured calorimetrically the reaction heat, which was evolved periodically in relation to the oscillations of the catalyst concentration. Stroot and coworkers[7] studied the B.–Zh. reaction with fluorinated 2,4-pentanedione, 2,5-hexanedione and acetone; they stated that the system oscillated even when the organic component did not contain a methylene group. Körös and coworkers[8] compared the B.–Zh. oscillating systems containing either malonic acid or 2,4-pentanedione and concluded that the Field–Körös–Noyes mechanism cannot be applied to the latter case. Rastogi and coworkers[9] compared the oscillating systems containing Ce^{4+} or Mn^{3+} ions as catalysts and malonic acid, citric acid, or 2,4-pentanedione as substrate, and substantiated the principal role of Br^- ions. Heilweil and Epstein[10] recently discovered a new phenomenon in the B.–Zh. system with 2,4-pentanedione: after the damped oscillations are finished, the concentration of Br^- ions remains constant for a certain time, after which irregular fluctuations in their concentration are observed. Their course varies from one experiment to another and resembles a "chaotic" behaviour of the system according to Rössler[11].

Oxidation of 2,4-pentanedione with $IrCl_6^{2-}$ ions was studied by Cecil and coworkers[12]: the reaction order is 1 with respect to both reactants and the reaction consists of two one-electron steps. In the first one, the anion of the enol form reacts under formation of a free radical. The formation of free radicals in the oxidation of 2,4-pentanedione with Ce(IV) ions was proved by the EPR method in a flow-through system[13]. A photoinduced oxidation of this substrate with V(V) ions leads to formic acid[14]. Oxidation of 2,4-pentanedione with H_2O_2 in the presence of Mo(VI) or W(VI) proceeds[15] in the coordination sphere of the transition metal under splitting of the C—C bond between the central C atom and acetal group; the final product is acetic acid and CO_2.

The oxidation of 2,4-pentanedione with Ce(IV) ions, an important reaction of the modified B.–Zh. oscillating system, has not been studied in detail and is dealt with in the present work.

EXPERIMENTAL

The kinetics of oxidation of 2,4-pentanedione with Ce(IV) ions was studied polarographically. The time dependence of the limiting diffusion current of Ce(IV) ions on a rotating Pt electrode was recorded at $-0{\cdot}05$ V *vs* Hg/Hg_2SO_4 in 2M-H_2SO_4. The experimental setup was described earlier[2].

Spectrophotometric measurements were carried out on a Specord UV-VIS type apparatus (Carl Zeiss, Jena) in 10 mm cuvettes placed in a tempered block connected with a TB 150 type ultrathermostat (Medingen). The reaction course was indicated by the time change of the absorbancy at 320 nm, the absorption maximum of Ce(IV) ions. The values of the rate constants are averages from four measurements.

The chemicals were of reagent grade, 2,4-pentanedione (Reachim, USSR) was redistilled. Solutions were prepared in redistilled water.

RESULTS

Kinetics of Oxidation of 2,4-*Pentanedione with* Ce(IV) *Ions*

The integral method showed that the oxidation of 2,4-pentanedione with Ce(IV) ions is a reaction of the first order with respect to both Ce(IV) ions and substrate. The dependence of the logarithm of the diffusion current of Ce(IV) ions on time is linear during the first two half-times of the reaction. The rate constant determined from the slope is directly proportional to the concentration of 2,4-pentanedione. The second-order rate constant is $k = 1{\cdot}5 \,.\, 10^2 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ in 1M-H_2SO_4 at 20°C. We measured the influence of the temperature on the reaction rate both in nitrogen and air atmosphere (Fig. 1). The activation enthalpy and entropy are $\Delta H^{\neq} = 46{\cdot}9 \text{ kJ} \,.\, \text{mol}^{-1}$, $\Delta S^{\neq} = -44 \text{ J K}^{-1} \text{ mol}^{-1}$ in the atmosphere of nitrogen, whereas $\Delta H^{\neq} = 51{\cdot}8 \text{ kJ mol}^{-1}$ and $\Delta S^{\neq} = -30 \text{ J K}^{-1} \text{ mol}^{-1}$ in the air atmosphere.

The experimental rate constant increases linearly with increasing concentration of H_3O^+ ions: $k_{exp} = k_{H^+}[H_3O^+]$ passing through the origin of coordinates. The slope of this straight line, $k_{H^+} = 0{\cdot}018 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ at 20°C, is equal to the catalytic constant in an excess of the substrate. With increasing ionic strength, the rate constant diminishes. The dependence of log k on $\sqrt{I}/(1 + \sqrt{I})$ is linear with a slope of $-1{\cdot}5$ in the interval of ionic strength $1-3$. The value of k_{exp} decreases also with increasing concentration of HSO_4^- ions at constant I and concentration of H_3O^+

ions, as illustrated in Table I. The reaction rate decreases with increasing initial concentration of Ce(III) ions (Table II). The dependence of k_{exp} on reciprocal concentration of Ce(III) ions is linear. From polarometric titration of Ce(IV) ions with a substrate solution it follows that two Ce(IV) ions are consumed per one 2,4-pentanedione molecule.

B.–Zh. Oscillating Reaction with 2,4-Pentanedione as Substrate

This reaction was recently studied by us polarographically[4]. After an induction period, the concentration of Ce(IV) ions begins to oscillate with an increasing amplitude, as proved also spectrophotometrically (Fig. 2). These oscillations take place also in the absence of stirring of the reacting solution. The influence of the temperature on the induction period of the oscillations was studied at the initial concentrations 0·06 mol/dm^3 $KBrO_3$, 6 . 10^{-3} mol/dm^3 2,4-pentanedione, and 4 . 10^{-4} mol/dm^3 $Ce(SO_4)_2$ in 1·5M-H_2SO_4. The logarithmic dependence of the induction period on reciprocal absolute temperature leads to the activation energy E = 82·2 kJ/mol and pre-exponential term A = 1·3 . 10^{12} s^{-1}. From the polarographic measurement of this dependence we obtained[4] E = 83·1 kJ/mol which is close to the mentioned value.

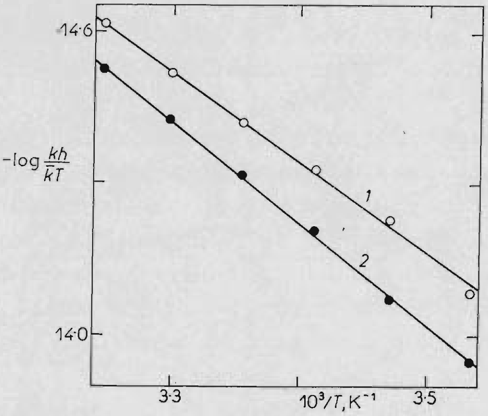

FIG. 1

Influence of oxygen on the temperature dependence of rate constant. 3·3 . 10^{-4} mol/dm^3 $Ce(SO_4)_2$, 4·7 . 10^{-4} mol/dm^3 2,4-pentanedione, 1 mol/dm^3 H_2SO_4. *1* In nitrogen atmosphere, 2 in air atmosphere

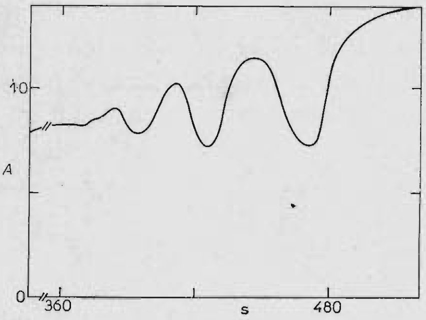

FIG. 2

Spectrophotometric record of B.–Zh. reaction with 2,4-pentanedione. 4 . 10^{-4} mol/ /dm^3 $Ce(SO_4)_2$, 6 . 10^{-3} mol/dm^3 2,4-pentanedione, 0·06 mol/dm^3 $KBrO_3$, 1·5 mol/ /dm^3 H_2SO_4, 20°C, λ = 320 nm

DISCUSSION

Our results are in accord with the following rate equation:

$$-\frac{d[Ce(IV)]}{dt} = \frac{k[Ce(IV)]\,[CH_3COCH_2COCH_3]\,[H_3O^+]}{[Ce(III)]\,[HSO_4^-]^{1/2}} \qquad (1)$$

and with a reaction mechanism according to which the enol form of 2,4-pentanedione forms an intermediate complex with $Ce(SO_4)_2$

$$Ce(SO_4)_2 + \text{enol} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ce(SO_4)_2 \,.\, \text{enol}\,, \qquad (a)$$

TABLE I

Dependence of experimental rate constant on concentration of HSO_4^- ions. 3·3 . 10^{-4} mol/dm^3 $Ce(SO_4)_3$, 4 . 10^{-4} mol/dm^3 2,4-pentanedione, 2 mol/dm^3 H_2O^+, 20°C

$c_{HSO_4^-}$, mol dm^{-3}	k_{exp} . 10^2, s^{-1}
0·25	11·0
0·50	8·0
0·75	6·6
1·00	5·6
1·50	4·7

TABLE II

Dependence of experimental rate constant on initial concentration of Ce(III) ions. 3·3 . 10^{-4} mol/dm^3 $Ce(SO_4)_2$, 4·7 . 10^{-4} mol/dm^3 2,4-pentanedione, 1 mol/dm^3 H_2SO_4, 20°C

$c_{Ce_2(SO_4)_3}$, mol dm^{-3}	k_{exp} . 10^2, s^{-1}
—	6·6
3·3 . 10^{-4}	3·2
6·6 . 10^{-4}	1·8
9·9 . 10^{-4}	1·1
2·0 . 10^{-3}	0·7
3·0 . 10^{-3}	0·4
5·0 . 10^{-3}	0·3

whose decomposition is the rate-determining (slow) step

$$\mathrm{Ce(SO_4)_3\,.\,enol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{R^{\bullet}} + \mathrm{Ce(SO_4)_2^-}\,. \tag{b}$$

Next step leads to a conversion of the radical $R^{\bullet}$

$$\mathrm{R^{\bullet}} + \mathrm{Ce(SO_4)_3^{2-}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{P} + \mathrm{Ce(SO_4)_2^-} + \mathrm{HSO_4^-}\,. \tag{c}$$

Solutions of Ce(IV) ions in sulphuric acid are characterized by the following mobile equilibria[16]:

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

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

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

The formation of free radicals during oxidation of 2,4-pentanedione with Ce(IV) ions was proved by Russel and coworkers using the EPR method[13]. The sum of the individual steps gives a stoichiometric equation whose coefficients were verified by polarometric titration. Based on the equilibrium constants[16] $K_1' = 3\,500$, $K_2' = 200$, and $K_3' = 20$, we can consider the following condition in the medium of $1\text{M-H}_2\text{SO}_4$:

$$[\mathrm{Ce(IV)}] \approx [\mathrm{Ce(SO_4)_3^{2-}}]\,. \tag{2}$$

According to the proposed reaction scheme, we have

$$\begin{aligned} -\mathrm{d}[\mathrm{Ce(SO_4)_3^{2-}}]/\mathrm{d}t &= k_2[\mathrm{Ce(SO_4)_2\,.\,enol}] = \\ &= k_2 K_1 T_\mathrm{T}[\mathrm{keto}][\mathrm{Ce(SO_4)_2}]\,, \end{aligned} \tag{3}$$

where K_T is the tautomeric equilibrium constant and K_1 corresponds to step (*a*). If we consider the step (*f*) and set the equilibrium concentration of the keto form equal to that of the substrate, we obtain

$$k_\mathrm{exp} = \frac{k_2 K_1 T_\mathrm{T}[\mathrm{CH_3COCH_2COCH_3}][\mathrm{H^+}]}{K_3'[\mathrm{HSO_4^-}]}\,. \tag{4}$$

This corresponds well to the mentioned results. The minus first reaction order with respect to Ce(III) ions shows that step (*b*) in the reversed direction comes probably into play at higher initial concentrations of Ce(III) ions.

Oxygen present in the reacting system retards the reaction as follows from the increase of the activation enthalpy by 4·9 kJ/mol. Such an effect was also observed by Cecil and Littler[12] in the oxidation of 2,4-pentanedione with $IrCl_6^{2-}$ ions and it can be elucidated in both cases by consumption of intermediate radicals reacting with oxygen molecules.

As mentioned above, the modified B.–Zh. reaction with 2,4-pentanedione is remarkable in that increasing oscillations are formed after the induction period even in the absence of stirring. The spectrometric kinetic measurements are in accord with the polarographic ones with a rotating platinum electrode. The oscillations have a peculiar character which, in accord with other authors[8], cannot be explained by the F.K.N. mechanism. It will be necessary to formulate a reaction scheme leading to differential equations, some of which will be nonlinear, their trajectories will have an unstable focus, and the real part of their complex roots will be positive[17]. The backward step (*b*) is probably essential: the reaction of Ce(III) ions with intermediate radicals which is important at higher concentrations of Ce(III) ions (in a later stage of the reaction). A thorough study of the modified B.–Zh. oscillating system with substrates similar to 2,4-pentanedione may enable to propose such a new reaction scheme.

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Translated by K. Micka.