Kinetic study of oxidation of glyceraldehyde by the cerium(IV) ions

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The kinetics and mechanism of oxidation of glyceraldehyde by cerium(IV) sulfate in a solution of sulfuric acid were studied. The reaction is a first-order reaction with respect to concentration of the Ce(IV) ions as well as with respect to concentration of the substrate. The value of experimental rate constant nonlinearly decreases with increasing concentration of the HSO_4^- ions. It also decreases after addition of the Ce(III) ions. The activation enthalpy ($\Delta H^+ = 78.1\,kJ\,mol^{-1}$) and the activation entropy ($\Delta S^+ = -33\,J\,K^{-1}\,mol^{-1}$) were evaluated from the temperature dependence of the rate constant by using the Eyring equation.

The probable reaction mechanism is discussed. It is assumed that the reaction proceeds through an intermediary complex the intramolecular decay of which is the rate-determining step. In the subsequent step the intermediary radical is attached by another Ce(IV) ion.

Изучена кинетика и механизм окисления глицеральдегида сульфатом церия(IV) в растворе серной кислоты. Реакция имеет первый порядок по ионам Ce(IV) и первый порядок по субстрату. Величина опытной константы скорости нелинейно уменьшается с увеличением концентрации ионов HSO_4^-, а также снижается после прибавления ионов Ce(III). Исходя из температурной зависимости константы скорости, с помощью уравнения Эйринга были определены значения энтальпии активации $\Delta H^+ = 78,1$ кДж моль$^{-1}$ и энтропии активации $\Delta S^+ = -33$ Дж К$^{-1}$ моль$^{-1}$.

Обсуждается вероятный механизм реакции, в соответствии с которым реакция протекает через промежуточный комплекс, внутримолекулярное разложение которого является скоростьопределяющей стадией. На второй стадии промежуточный радикал атакуется следующим ионом Ce(IV).

At present, the kinetics and mechanism of oxidation of organic substrates by the Ce(IV) ions are given great attention in connection with the complex investigation of the Belousov—Zhabotinskii oscillating reaction because the oxidation of substrate by the oxidized component of the redox catalyst is one

of the three main processes in this oscillating reaction [1]. Since glyceraldehyde (2,3-dihydroxypropanal) has not yet been used as a substrate in the Belousov —Zhabotinskii reaction and the kinetics of its oxidation by the Ce(IV) ions has not been investigated, this study is aimed at kinetic study of the mechanism of this reaction.

Experimental

The kinetics of oxidation of glyceraldehyde 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 $\lambda_{max} = 320$ 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).

Cerium(IV) sulfate (VEB Laborchemie), DL-glyceraldehyde (Fluka, Buchs), other chemicals, and solvents used for the preparation of solutions were anal. grade chemicals.

The values of rate constants obtained in this study are mean values of three measurements carried out within accuracy of ± 3 %. The stoichiometry of the reaction was determined by photometric titration.

Results

The redox reaction of the Ce(IV) ions with glyceraldehyde in 0.2 M solution of sulfuric acid at 20 °C is a reaction of the first order with respect to the Ce(IV) ions as well as with respect to the substrate. The experimental rate constant is a linear function of the substrate concentration within the concentration range from 2.5×10^{-3} to 2.5×10^{-2} mol dm^{-3} (Fig. 1). The slope of the linear relationship of the rate constant to
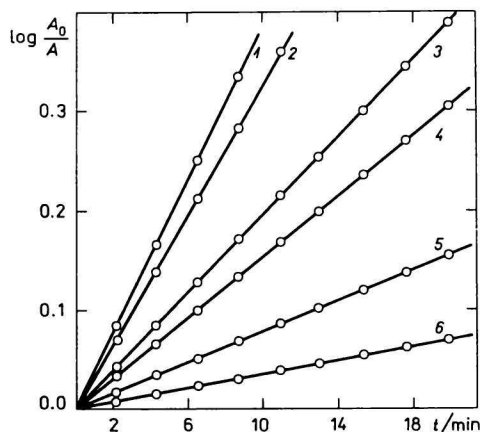

Fig. 1. Experimental evidence of the first-order kinetics with respect to Ce(IV).
0.2 M-H_2SO_4, 2.5×10^{-4} M-Ce(SO$_4$)$_2$, c(glyceraldehyde)/(mol dm^{-3}): 1. 2.5×10^{-2}; 2. 2.0×10^{-2}; 3. 1.25×10^{-2}; 4. 1.0×10^{-2}; 5. 5×10^{-3}; 6. 2.5×10^{-3}. $\theta = 20$ °C.

Table 1

Variation of the experimental rate constant with concentration of substrate
0.2 M-H$_2$SO$_4$, 2.5 × 10^{-4} M-Ce(SO$_4$)$_2$, $\theta = 20$ °C

Concentration of glyceraldehyde $c \cdot 10^3/(\text{mol dm}^{-3})$	2.5	5.0	10.0	12.5	20.0	25.0
Experimental rate constant $k_{exp} \cdot 10^4/\text{s}^{-1}$	1.34	2.96	5.84	7.50	12.65	14.51

the concentration of glyceraldehyde gives the value of the rate constant k_2 ($k_2 = 5.95 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}) (Table 1). The values of activation enthalpy $\Delta H^{\pm} = 78.1$ kJ mol^{-1} and activation entropy $\Delta S^{\pm} = -33$ J K^{-1} mol^{-1} were determined on the basis of the temperature dependence of rate constant by using the Eyring equation (Fig. 2).

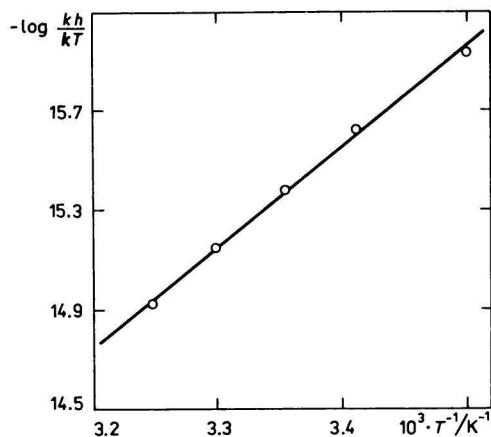Fig. 2. Variation of the rate constant with temperature.
0.2 M-H$_2$SO$_4$, 2.5 × 10^{-4} M-Ce(SO$_4$)$_2$,
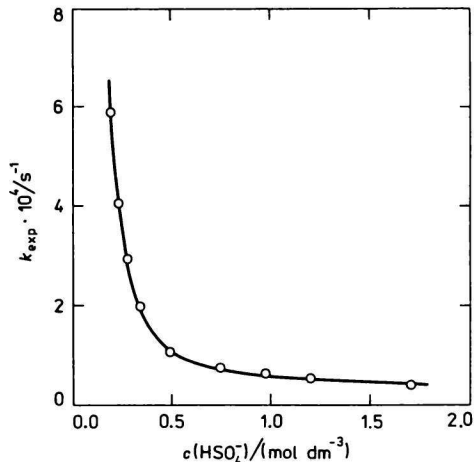2.5 × 10^{-2} M glyceraldehyde.

Fig. 3. Variation of the experimental rate constant with concentration of the HSO$_4^-$ ions.
2.5 × 10^{-4} M-Ce(SO$_4$)$_2$, 1.25 × 10^{-2} M glyceraldehyde; $\theta = 20$ °C, $I = 1.7$ mol dm^{-3} (ionic strength adjusted with an appropriate addition of NaClO$_4$).

The investigated reaction is catalyzed by the H$_3$O$^+$ ions. The logarithm of the experimental rate constant is a linear function of concentration of the H$_3$O$^+$ ions (Table 2). At constant concentration of the H$_3$O$^+$ ions and constant value of the ionic strength the value of the experimental rate constant nonlinearly decreases with increasing concentration of the HSO$_4^-$ ions (Fig. 3). The dependence of the experimental rate

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Table 2

Variation of the experimental rate constant with concentration of the H_3O^+ ions
0.2 M-H_2SO_4, 2.5×10^{-4} M-Ce(SO$_4$)$_2$, 1.25×10^{-2} M glyceraldehyde;
I(NaClO$_4$) = 1.2 mol dm^{-3}, $\theta = 20\,^{\circ}$C

| $c_{H_3O^-}$(mol dm^{-3})	0.2	0.45	0.7	0.95	1.2
$k_{exp} \cdot 10^4$ s^{-1}	0.72	0.93	1.20	1.61	2.21

Table 3

Variation of the experimental rate constant with ionic strength
0.2 M-H_2SO_4, 2.5×10^{-4} M-Ce(SO$_4$)$_2$, 1.25×10^{-2} M glyceraldehyde; $\theta = 20\,^{\circ}$C, ionic strength was adjusted with NaClO$_4$

I (mol dm^{-3})	0.2	0.575	0.95	1.325	1.7
$k_{exp} \cdot 10^4$ s^{-1}	8.58	7.98	7.44	6.53	5.58

constant on ionic strength is linear, the slope being -1.87×10^{-4} (Table 3). An addition of the Ce(III) ions into the solution reduces the reaction rate. The value of the experimental rate constant at c(Ce$_2$(SO$_4$)$_3$) = 2.5×10^{-4} mol dm^{-3} and c(Ce$_2$(SO$_4$)$_3$) = 6.2×10^{-4} mol dm^{-3} was reduced by 10 % and 17 %, respectively. The reaction stoichiometry corresponds to consumption of two Ce(IV) ions per one molecule of the substrate.
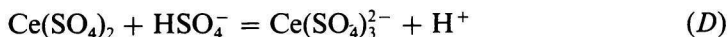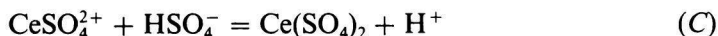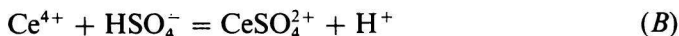
Discussion

The described results of kinetic study of the oxidation of glyceraldehyde by the Ce(IV) ions may be interpreted on the basis of assumption of the intermediary complex

$$\text{HO—CH}_2\text{—CH—CH} \qquad (A)$$
$$\underset{\overset{\cdots}{\text{Ce(IV)}}}{\overset{|}{\text{OH}}}\;\overset{||}{\underset{\cdots}{\text{O}}}$$
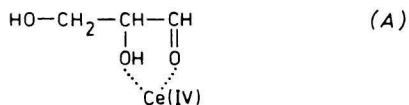
the decay of which is a slow and thus rate-determining step of the redox reaction. The decay of the intermediary complex is an intramolecular redox step which gives rise to the intermediary radical HOCH$_2$—$\dot{\text{C}}$(OH)—CHO and Ce(III) ion. The generation of this intermediary complex was postulated in the nonkinetic study by *Kurlyankina et al.* [2, 3] who evidenced the formation of the above-mentioned free radical with unpaired electron on carbon atom by using the EPR method in a flow system. The negative value of the obtained activation entropy $\Delta S^{\ddagger} = -33\,$J K^{-1} mol^{-1} corresponds to the decrease in degrees of

freedom accompanying the transfer from initial state to transition state. If the observed inhibitory effect of the Ce(III) ions is taken into consideration, the reaction step involving the decomposition of the intermediary complex into the Ce(III) ion and radical may be regarded as a reversible process. In the second step of the redox reaction the radical is attached by the second Ce(IV) ion, which results in formation of the final oxidation product. According to Ref. [2], the presence of glyoxal, hydroxymethylglyoxal, and formic acid was proved in the reaction mixture after completion of the reaction. The proportion of reaction products is dependent on the proportion of reactants. *Barek et al.* [4] were concerned with the oxidation of glyceraldehyde by the Mn(III) ions. They observed that not only formic acid but also formaldehyde originated in the reaction mixture.

The nonlinear decrease in the value of rate constant with increasing concentration of the HSO_4^- ions (Fig. 3) suggests a successive formation of cerium(IV) complexes with increasing number of the coordinated SO_4^{2-} ions in line with the scheme according to *Hardwick* and *Robertson* [5] as described in our earlier papers, *e.g.* [6].

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

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

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

The influence of the H_3O^+ ions on reaction rate (Table 2) may be due to a shift in equilibrium (D) in favour to $Ce(SO_4)_2$ which enters into reaction in the first step giving rise to intermediary complex (A). A small influence of ionic strength on the value of experimental rate constant (Table 3) is in agreement with the idea that a noncharged particle $Ce(SO_4)_2$ enters into reaction in the first step. In the sense of eqns $(B—D)$ the equilibrium shifts in favour of the less reactive particle $Ce(SO_4)_3^{2-}$ and to the detriment of the particle $Ce(SO_4)_2$ with increasing concentration of the HSO_4^- ions at constant value of $[H_3O^+]$ and ionic strength, and, for this reason, the value of experimental rate constant decreases.

The results obtained by investigating the above-mentioned redox reaction suggest that glyceraldehyde might be a convenient substrate of the oscillating reaction of the Belousov—Zhabotinskii type, which will be the topic of the following paper.

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