

Kinetics and mechanism of oxidation of 2,4-pentanedione by the manganese(III) ions

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Received 8 April 1982

The oxidation of 2,4-pentanedione by the Mn(III) ions in the solution of sulfuric acid is an inner-sphere reaction which proceeds *via* intermediary complexes. The reaction is a first-order reaction with respect to concentration of the Mn(III) ions even if the concentrations of both reactants are equal. The experimental rate constant $k_{\text{exp}}/\text{s}^{-1}$ increases initially linearly and subsequently nonlinearly with concentration of the substrate, reaches the maximum value and afterwards it decreases. A plausible reaction mechanism was proposed according to which the slow and rate-determining step is an intramolecular redox reaction of the intermediary Mn—Enol complex or of the less reactive Mn—(Enol)₂ complex.

The temperature dependence of the experimental rate constant was used for evaluating the activation parameters, *i.e.* activation enthalpy and activation entropy which were also dependent on temperature. On the basis of temperature dependence of these parameters, the activation heat capacities $\Delta C_p^* = -1.4 \text{ kJ mol}^{-1} \text{ K}^{-1}$ in the presence of oxygen and $\Delta C_p^* = -2.2 \text{ kJ mol}^{-1} \text{ K}^{-1}$ in nitrogen atmosphere were calculated.

Окисление 2,4-пентандиона ионами Mn(III) в растворе серной кислоты является внутрисферной реакцией, проходящей с образованием промежуточных комплексов. Реакция протекает по первому порядку относительно концентрации ионов Mn(III) даже при равных концентрациях обоих реагентов. Экспериментальная константа скорости $k_{\text{эксп}}/\text{с}^{-1}$ с возрастанием концентрации субстрата сначала растет линейно, затем нелинейно, достигает максимального значения и затем убывает. Предложен возможный механизм реакции, в соответствии с которым медленной и скорость определяющей стадией является внутримолекулярная окислительно-восстановительная реакция промежуточного комплекса Mn—Енол или менее реакционноспособного Mn—(Енол)₂.

На основании температурной зависимости экспериментальной константы скорости были оценены активационные параметры — энтальпия и энтропия активации, также зависящие от температуры, а на основе их температурных зависимостей были рассчитаны активационные теплоем-

кости $\Delta C_p^* = -1,4 \text{ кДж моль}^{-1} \text{ K}^{-1}$ в присутствии кислорода и $\Delta C_p^* = -2,2 \text{ кДж моль}^{-1} \text{ K}^{-1}$ в атмосфере азота.

As a rule, the Mn(III) ions oxidize those aldehydes and ketones which are able to form the enol form [1—3]. In these cases, the reaction is of the zero order with respect to concentration of the Mn(III) ions and of the first order with respect to concentration of the H_3O^+ ions. In conformity with this observation, a reaction mechanism was put forward according to which the slow and rate-determining step is the acid-catalyzed enolization which precedes the oxidation of the enol form. On the other hand, it has been observed [4—12] that the oxidation of some aldehydes and ketones is a reaction of the first order with respect to the Mn(III) ions and, for this reason, we may assume a direct attack of the Mn(III) ions on the keto form of substrate giving rise to an intermediary complex. In either case, the intermediary complex decomposes and produces an intermediary radical which is attacked in subsequent step by another Mn(III) ion.

The kinetics of oxidation of 2,4-pentanedione by the Mn(III) ions which is important from the view-point of complex study of the Belousov—Zhabotinskii reaction [13—15] has not been thoroughly described in literature by now and, for this reason, it was chosen to be the topics of this study.

Experimental

The kinetics of oxidation of 2,4-pentanedione by the Mn(III) ions was studied polarographically by investigating the time dependence of the limiting diffusion current of the Mn(III) ions on the dropping mercury electrode at the potential of -0.2 V against the potential of $\text{Hg}|\text{Hg}_2\text{SO}_4$ in $1.5 \text{ M-H}_2\text{SO}_4$. The present values of rate constants are average of four independent measurements at least.

The solution of the Mn(III) ions was prepared by 10 min electrooxidation of $5 \times 10^{-4} \text{ M-MnSO}_4$ in $1.5 \text{ M-H}_2\text{SO}_4$ on a large surface platinum electrode in nitrogen atmosphere (electric bulb industry nitrogen).

The used chemicals were anal. grade reagents. 2,4-Pentanedione (Reakhim, the USSR) was redistilled. All solutions were prepared with redistilled water.

The values of activation parameters were evaluated by the procedure described in paper [16].

Results

The kinetics of oxidation of 2,4-pentanedione by the Mn(III) ions was studied in solutions of $1.5 \text{ M-H}_2\text{SO}_4$. These solutions are usually used for investigating the

course of the Belousov—Zhabotinskii reaction involving 2,4-pentanedione as substrate [13—15]. The reaction is of the first order with respect to the Mn(III) ions because the dependence of logarithm of the limiting diffusion current of the Mn(III) ions on time is linear in the first two half-life periods. The value of diffusion current was determined in comparison to its value after the third half-life period of reaction. The value of the rate constant $k_{\text{exp}}/\text{s}^{-1}$ was determined from the slope of kinetic curve. The first reaction order with respect to concentration of the Mn(III) ions was observed even if the initial concentrations of both reactants were equal ($5 \times 10^{-4} \text{ mol dm}^{-3}$). The reaction order with respect to concentration of the substrate is more intricate because the experimental rate constant k_{exp} increases at the outset linearly and subsequently nonlinearly with substrate concentration reaches its maximum value and afterwards it decreases (Fig. 1). The value of the

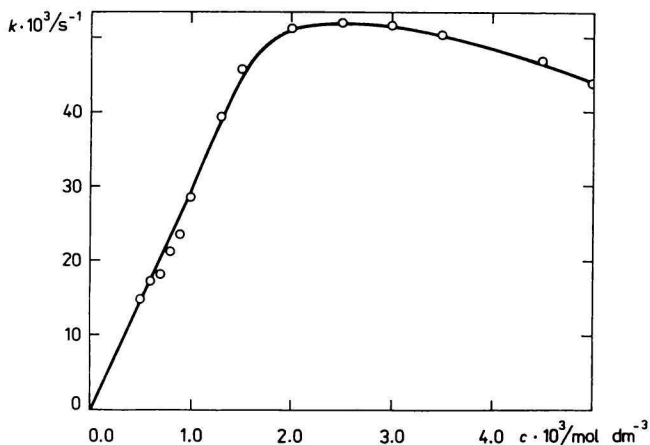


Fig. 1. Variation of the experimental rate constant with concentration of 2,4-pentanedione. $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$; $[\text{Mn(III)}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $\theta = 5^\circ\text{C}$.

experimental rate constant does not change with concentration of the H_3O^+ ions within the concentration range $1.5\text{—}5.0 \text{ mol dm}^{-3}$. Similarly, it does not change with ionic strength in the ionic strength interval between 1.5 mol dm^{-3} and 4.0 mol dm^{-3} .

Special attention was given to the study of the temperature dependence of the rate constant in the presence and in the absence of oxygen. The dependence of logarithm of the numerical value of rate constant on reciprocal value of absolute temperature is not linear in broader temperature interval (Fig. 2). It results from this fact that the values of activation enthalpy as well as activation entropy depend on temperature (Table 1). From the temperature dependence of activation enthalpy we determined the value of activation heat capacity for which we obtained

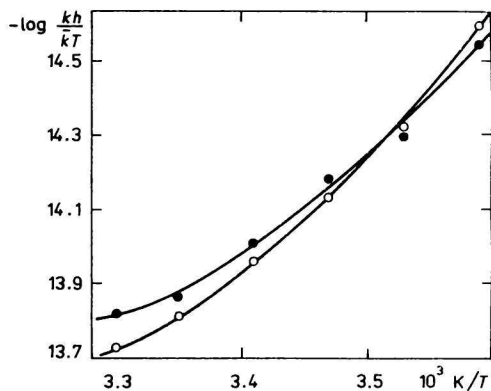


Fig. 2. Variation of the experimental rate constant with temperature.

$[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$; $[\text{Mn(III)}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{2,4-pentanedione}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$.

● In the presence of oxygen; ○ in nitrogen atmosphere.

Table 1

Temperature dependence of activation enthalpy and activation entropy
 $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$; $[\text{Mn(III)}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{2,4-pentanedione}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$

T/K	$\Delta H^\ddagger/\text{kJ mol}^{-1}$		$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	
	with O_2	without O_2	with O_2	without O_2
283.2	57.1	74.4	- 72	- 11
288.2	45.2	57.6	-115	- 71
293.2	50.2	51.1	- 97	- 93
298.2	33.0	39.3	-155	-133

$\Delta C_p^\ddagger = -1.4 \text{ kJ mol}^{-1} \text{K}^{-1}$ in the presence of oxygen and $\Delta C_p^\ddagger = -2.2 \text{ kJ mol}^{-1} \text{K}^{-1}$ in nitrogen atmosphere.

The reaction stoichiometry was ascertained by polarometric titration of 2,4-pentanedione with the Mn(III) ions. It appeared that two Mn(III) ions were consumed for one substrate molecule.

Discussion

On the basis of the described results we may assume the subsequent reaction mechanism. The dependence of the rate constant on concentration of 2,4-pentanedione has the character resembling the pertinent dependence valid for enzyme reactions with two or several intermediary complexes the reactivity of which decreases with the number of coordinated substrates [17]. The oxidation of

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Translated by R. Domanský