

OSCILLATIONS OF THE ENOL FORM OF 2,4-PENTANEDIONE DURING BELOUSOV-ZHABOTINSKII REACTION

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In the Belousov-Zhabotinskii oscillation reaction with 2,4-pentanedione and Mn^{2+}/Mn^{3+} redox catalyst, also the enol form of the substrate has an oscillating concentration. The decrease of the concentration of the enol form is due to its reaction with bromine and Mn^{3+} ions; its increase corresponds to the reestablishment of the keto-enol equilibrium, when the concentrations of bromine and Mn^{3+} ions are low. An oscillating time-course was observed also with the concentration of the intermediate product of the reaction, of 2,4-pentanedione with Mn^{3+} ions, probably an intermediate complex [Mn(III)-enol], which oscillated with a phase shift against Mn^{3+} ions.

The modified Belousov-Zhabotinskii reaction in the presence of 2,4-pentanedione as substrate was studied by many authors. Bowers and coworkers¹ showed that no gaseous products are evolved in this reaction, which can proceed in a closed system. Janjic and coworkers² studied potentiometrically oscillations of Br^- and Ce^{3+}/Ce^{4+} ions in the system $Ce^{4+}/KBrO_3/2,4$ -pentanedione. They measured the reaction heat effect calorimetrically and found a periodic heat formation in relation to the concentration oscillations of the catalyst. Stroot and coworkers³ studied the B.-Zh. reaction with fluorinated 2,4-pentanedione, 2,5-hexanedione, and acetone; they proved that the system oscillates even if the organic substrate contains no methylene group. Körös and coworkers⁴ compared the B.-Zh. oscillation systems containing either malonic acid or 2,4-pentanedione and arrived at the conclusion that the Field-Körös-Noyes mechanism cannot be applied to the system with the latter compound. Rastogi and coworkers⁵ studied the oscillation systems with Ce^{4+} or Mn^{3+} ions as catalyst and malonic acid, citric acid, or 2,4-pentanedione as substrate; they substantiated the important role of Br^- ions. Heilweil and Epstein⁶ reported a new phenomenon in the B.-Zh. system with 2,4-pentanedione: After finishing the damped oscillations, the concentration of Br^- ions remains constant for some time and then irregular, random fluctuations of the concentration take place. These differ in their course from one experiment to another resembling a chaotic behaviour according to Rössler⁷. The polarographic and spectrophotometric studies of the mentioned system were reviewed by us^{8,9}.

Recently, Rastogi and Rastogi¹⁰ described an oscillating behaviour of the system $Mn^{2+}/NaBrO_3/2,4$ -pentanedione in a solution of sulphuric acid. They observed that Mn^{3+} and Br^- ions oscillated in the same phase, while the temperature increased periodically. We observed in the present work that also the concentrations of the enol form 2,4-pentanedione and of an intermediate complex are subject to oscillations in the indicated system.

EXPERIMENTAL

The kinetics and course of the reactions were followed by means of a UV-VIS type spectrophotometer (Carl Zeiss, Jena). This method is suitable mainly because the B.-Zh. system with 2,4-pentanedione oscillates already without stirring and does not evolve gaseous products¹. Cuvettes of a thickness of 1–50 mm were placed in a tempered block connected with an ultrathermostat and were provided with a stopper with a glass capillary connected with a syringe. The injection method was used and the solution was stirred by a magnetic stirrer during recording. The rate of attainment of the tautomeric equilibrium of 2,4-pentanedione was measured by injecting the vapour of this substance into the solution and recording the time dependence of the absorbancy of the enol form at $\tilde{\nu} = 36\,000\text{ cm}^{-1}$ (ref.^{11,12}). The experimental rate constant is $k_{\text{exp}} = k_{\text{E}} + k_{\text{K}}$, where k_{E} refers to enolization and k_{K} to the back reaction. The kinetics of the increasing portion of the enol form oscillation was evaluated by the Guggenheim method using the relation $\ln(A_t - A_{t+\tau}) = k_{\text{G}}t$, where τ is a constant time interval.

The absorption spectrum of the intermediate product of the reaction of 2,4-pentanedione with Mn^{3+} ions was recorded by the flow-through method using a quartz glass 10 mm cuvette. The rate of flow of the solution was $100\text{ cm}^3/\text{min}$; 2 s after mixing the solution arrived in the measuring region of the cuvette. The concentration of the enol form of 2,4-pentanedione in 1.5M- H_2SO_4 was determined spectrophotometrically at various temperatures and the measurements were referred to the absorbancy of 2,4-pentanedione in water at 25°C, where the enol form concentration was known¹¹.

The enolization measurements were repeated three times at lower temperatures and six times at higher ones. The value of k_{exp} was at lower temperatures subject to an error of $\pm 2\%$, at 35°C $\pm 5\%$, since the reaction rate is rather high at this temperature (the reaction half-time being less than a second). The rate constant k_{G} found from oscillation measurements by the Guggenheim method is subject to larger errors which also increase with the temperature (5–10%). To study the oscillation reaction, a solution of KBrO_3 was added, as the last component, to a solution of Mn^{2+} ions and 2,4-pentanedione in diluted sulphuric acid, whereby the reaction started.

Redistilled water and reagent grade chemicals were used. A solution of Mn^{3+} ions was prepared by mixing Mn^{2+} with MnO_4^- ions in 4.5M- H_2SO_4 in the ratio of 4 : 1 to 8 : 1. The concentrations were chosen in order that the resulting Mn^{3+} concentration in 4.5M- H_2SO_4 did not exceed $2 \cdot 10^{-3}\text{ mol/dm}^3$. The solution was diluted with 1 : 3 with redistilled water prior to the measurement.

RESULTS

Spectrophotometric Record of Oscillation Reaction

As seen from Fig. 1, the absorption maximum of Mn^{3+} is at $20\,000\text{ cm}^{-1}$ and in the presence of bromine it can be measured in the region from $16\,000$ to $18\,000\text{ cm}^{-1}$. The absorption maximum of Br_2 is at $25\,000\text{ cm}^{-1}$, but its concentration changes could be measured only together with those of Mn^{3+} . 2,4-pentanedione gives an absorption maximum at $36\,400\text{ cm}^{-1}$ (Fig. 2) corresponding to its enol form^{11,13–15} ($\pi \rightarrow \pi^*$ transition in the system of conjugated double bonds). This is substantiated by the following facts: 1) The experimental value of λ_{max} agrees with that calculated for α, β -unsaturated diketones according to the Woodward–Fiesner rules; 2) the value

of λ_{\max} is shifted to shorter wave lengths on passing from a polar (H_2O) to a non-polar solvent (n-hexane); and 3) there is a linear increase of the absorbancy with the percentual content of the enol form when a less polar solvent is used¹¹. Bromate and Mn^{3+} ions and bromine also absorb in the UV region, however their molar absorption coefficients are by two orders of magnitude smaller and so it is possible to measure the enol form concentration without distortion by the background.

A spectrophotometric record of the oscillation reaction at various wave numbers is shown in Fig. 3. The changes of the absorbancy at $\tilde{\nu} = 18\,000\text{ cm}^{-1}$ correspond to concentration changes of Mn^{3+} in accord with polarography and the EPR method¹⁶⁻²⁰. The Mn^{3+} concentration varied in the interval 0–20% of the analytical Mn concentration. Doubled oscillations were observed at $\tilde{\nu} = 25\,000\text{ cm}^{-1}$; the first one of the couple corresponds to Mn^{3+} and the second one to an intermediate product which shows a phase shift with respect to Mn^{3+} . The rapid increase of absorbancy after the oscillations are finished corresponds to the evolved bromine, which was proved spectrophotometrically by its absorption maximum at $25\,000\text{ cm}^{-1}$. This maximum decreased by bubbling with an inert gas, and bromine carried

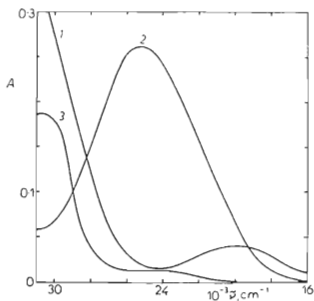


FIG. 1

Absorption spectra. 1 $6 \cdot 10^{-4}\text{ M-Mn}^{3+}$ in $1.5\text{ M-H}_2\text{SO}_4$; 2 $1.5 \cdot 10^{-3}\text{ M-Br}_2$; 3 intermediary complex formed in the reaction of 2,4-pentanedione with Mn^{3+} in $1.5\text{ M-H}_2\text{SO}_4$ (flow-through method). 10 mm cuvette, 25°C

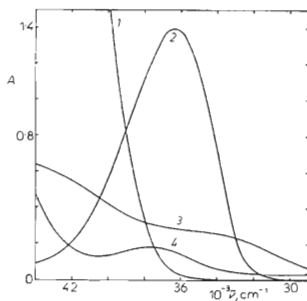


FIG. 2

Absorption spectra. 1 0.06 M-BrO_3^- ; 2 $8 \cdot 10^{-4}\text{ M}$ 2,4-pentanedione; 3 $2 \cdot 10^{-4}\text{ M-Mn}^{3+}$ in $1.5\text{ M-H}_2\text{SO}_4$; 4 $8 \cdot 10^{-4}\text{ M-Br}_2$. 10 mm cuvette, 25°C

away by the gas was proved analytically by its reaction with fluorescein. The oscillating absorbancy at $36\,000\text{ cm}^{-1}$ corresponds to the enol form of 2,4-pentanedione.

The character of the oscillation reaction depends on the initial concentrations of the reactants. Oxidation of 2,4-pentanedione is accelerated by increasing concentration of BrO_3^- and Mn^{2+} ions, whereby the oscillations last shorter, their number also decreases, but the amplitude of the oscillations of the enol form increases (Fig. 4). An increase of the initial concentration of 2,4-pentanedione (Fig. 5) causes the appearance of an induction period, the oscillation amplitude becomes much smaller, the oscillations are damped during the reaction, and the oxidation of the substrate proceeds without oscillations. In addition, the amplitude of the oscillations of Mn^{3+} decreases and bromine begins to evolve only when the substrate concentration drops to zero. Oscillations of the enol form with a large amplitude take place when the ratio of the initial concentrations of the substrate and Mn^{2+} is about 2 : 1. Under

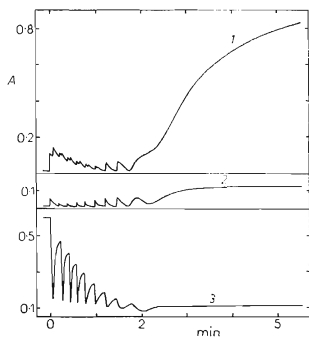


FIG. 3

Spectrophotometric record of oscillation reaction. $4 \cdot 10^{-3}\text{ M}$ 2,4-pentanedione, $2 \cdot 10^{-3}\text{ M}$ Mn^{2+} , $6 \cdot 10^{-2}\text{ M}$ BrO_3^- , 1.5 M H_2SO_4 ; 25°C . 1 $\tilde{\nu} = 25\,000\text{ cm}^{-1}$, 50 mm cuvette; 2 $\tilde{\nu} = 17\,600\text{ cm}^{-1}$, 50 mm cuvette; 3 $\tilde{\nu} = 36\,000\text{ cm}^{-1}$, 1 mm cuvette

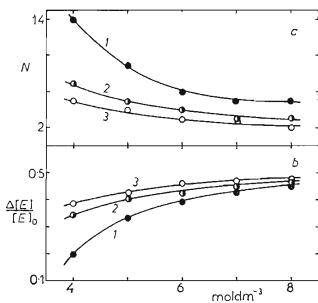


FIG. 4

Dependences of a) total number of oscillations N and b) amplitude of the first oscillation $\Delta[E]/[E]_0$ on initial concentration of Mn^{2+} ; $\Delta[E]$ is the maximum concentration change of the enol form in the 1st oscillation and $[E]_0$ is its initial (equilibrium) concentration. Base solution: $1.6 \cdot 10^{-3}\text{ M}$ 2,4-pentanedione and 1.5 M H_2SO_4 . 1 0.03 M BrO_3^- ; 2 0.045 M BrO_3^- ; 3 0.06 M BrO_3^- ; 25°C

this condition, the concentration of Mn^{3+} ions oscillates (except for the first period) with an increasing amplitude (Fig. 3). The oscillations of the enol form suggest that one or more reaction components (Mn^{3+} , Br_2) react preferentially with it, whereby its concentration decreases. Recovering of the enol form concentration is due to reestablishment of the keto-enol equilibrium.

Enolization of 2,4-Pentanedione

The enolization is acid-catalysed; the dependence of the experimental rate constant for the keto-enol equilibration, k_{exp} , on the concentration of sulphuric acid, c (Table I) can be linearized by plotting $\log \Delta k_{\text{exp}}$ against H_{ϕ} , where $\Delta k_{\text{exp}} = k_{\text{exp}}(c) - k_{\text{exp}}(0)$. The acidity function H_{ϕ} is equal to $\phi \log c - (1 - \phi) H_0$, where H_0 is the general acidity function and ϕ is the solvation constant¹⁶, equal to 0.62. The dependence of k_{exp} and of the fraction of the enol form, f_E , on the temperature is

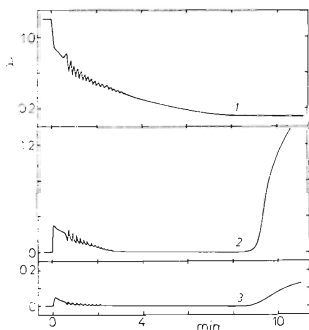


FIG. 5

Spectrophotometric record of oscillation reaction. $8 \cdot 10^{-3}\text{M}$ 2,4-pentanedione, $2 \cdot 10^{-3}\text{M-Mn}^{2+}$, $6 \cdot 10^{-2}\text{M-BrO}_3^-$, $1.5\text{M-H}_2\text{SO}_4$; 25°C . $1 \tilde{\nu} = 36\,000\text{ cm}^{-1}$, 1 mm cuvette; $2 \tilde{\nu} = 25\,000\text{ cm}^{-1}$, 50 mm cuvette; $3 \tilde{\nu} = 17\,600\text{ cm}^{-1}$, 50 mm cuvette

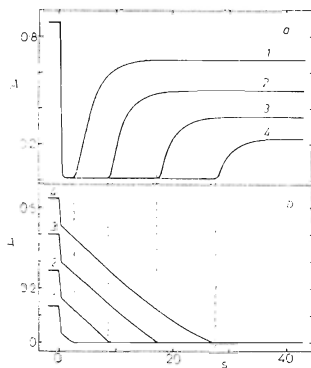


FIG. 6

Spectrophotometric record of reaction of 2,4-pentanedione with bromine. Base solution: $8 \cdot 10^{-4}\text{M}$ 2,4-pentanedione and $1.5\text{M-H}_2\text{SO}_4$ at 25°C . Initial bromine concentration: $1.18 \cdot 10^{-4}$; $2.36 \cdot 10^{-4}$; $3.54 \cdot 10^{-4}$; $4.72 \cdot 10^{-4}\text{ mol/dm}^3$. $a \tilde{\nu} = 35\,000\text{ cm}^{-1}$, 10 mm cuvette (enol form); $b \tilde{\nu} = 25\,000\text{ cm}^{-1}$, 50 mm cuvette (bromine)

given in Table II. The rate constants of enolization, k_E , and of ketonization, k_K , can be calculated as

$$k_E = k_{\text{exp}} f_E, \quad k_K = k_{\text{exp}}(1 - f_E). \quad (1)$$

TABLE I

Dependence of enolization rate and oscillations of the enol form of 2,4-pentanedione on H_2SO_4 concentration. The experimental rate constant k_{exp} refers to the keto-enol equilibration, k_G is that measured by the Guggenheim method from the rising portion of the oscillations of the enol form, $\Delta k_{\text{exp}} = k_{\text{exp}}(c) - k_{\text{exp}}(0)$, where c is the concentration of H_2SO_4 , H_Φ denotes acidity function

$[\text{H}_2\text{SO}_4]$ mol dm^{-3}	k_{exp} s^{-1}	$\log \Delta k_{\text{exp}}$	H_Φ	k_G s^{-1}
0.00	0.0965	—	—	—
0.25	0.137	-1.393	-0.541	—
0.50	0.172	-1.122	-0.236	—
0.75	0.208	-0.953	-0.051	—
1.00	0.259	-0.789	0.099	0.28
1.25	0.311	-0.669	0.220	0.32
1.50	0.374	-0.559	0.322	0.37
1.75	0.448	-0.453	0.417	0.44
2.00	0.563	-0.332	0.506	0.54

TABLE II

Dependence of enolization rate, fraction of enol form f_E and its oscillations on temperature. For meaning of k_{exp} and k_G see Table I; $k_E = k_{\text{exp}} f_E$, $k_K = k_{\text{exp}}(1 - f_E)$

T $^\circ\text{C}$	k_{exp} s^{-1}	k_G^a s^{-1}	k_G^b s^{-1}	k_G^c s^{-1}	f_E	$k_E \cdot 10^2$ s^{-1}	$k_K \cdot 10$ s^{-1}
15.0	0.162	0.17	0.15	0.16	0.139	2.26	1.39
20.0	0.252	0.26	0.24	0.25	0.133	3.35	2.18
25.0	0.374	0.36	0.35	0.38	0.127	4.76	3.26
30.0	0.534	0.52	0.51	0.56	0.122	6.52	4.69
35.0	0.800	0.83	0.87	0.76	0.117	9.35	7.06

^a $8 \cdot 10^{-4} \text{M-Mn}^{2+}$, first oscillation; ^b $8 \cdot 10^{-4} \text{M-Mn}^{2+}$, second oscillation; ^c $5 \cdot 10^{-4} \text{M-Mn}^{2+}$, 2nd–5th oscillations.

The results are given in Table II. The corresponding activation parameters were calculated from the temperature dependences of k_{exp} , k_{E} , and k_{K} with the aid of the Eyring equation:

$$\begin{aligned} \Delta H_{\text{exp}}^{\ddagger} &= 55.9 \text{ kJ/mol} & \Delta S_{\text{exp}}^{\ddagger} &= -70 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta H_{\text{E}}^{\ddagger} &= 49.3 \text{ kJ/mol} & \Delta S_{\text{E}}^{\ddagger} &= -105 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta H_{\text{K}}^{\ddagger} &= 56.3 \text{ kJ/mol} & \Delta S_{\text{K}}^{\ddagger} &= -66 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

Bromination of 2,4-Pentanedione

Changes in the enol form concentration during the reaction with Br_2 in 1.5M- H_2SO_4 are illustrated by Fig. 6a. With increasing Br_2 concentration, the time interval, t_{Br} , is prolonged during which the enol form concentration is very low and the Br_2 concentration decreases almost linearly to zero (Fig. 6b). Since $k_{\text{E}} \ll k_{\text{Br}}[\text{Br}_2]$, where k_{Br} denotes the rate constant for the reaction of the enol form with bromine¹⁷, the rate of bromination is given by that of the preceding enolization and the time t_{Br} depends on the initial concentrations of the reactants according to the equation

$$t_{\text{Br}} = \frac{1}{k_{\text{E}}} \ln \frac{[\text{P}]_0 (1 - f_{\text{E}})}{[\text{P}]_0 - [\text{Br}_2]_0}, \quad (2)$$

where $[\text{P}]_0$ is the initial concentration of 2,4-pentanedione, $[\text{Br}_2]_0$ that of bromine, k_{E} denotes the rate constant of enolization and f_{E} fraction of the enol form. The calculated and experimental values of k_{Br} are summarized in Table III. When the bromine concentration drops to zero, the keto-enol equilibrium is reestablished by enolization of the keto form (Fig. 6a). The first-order rate constants calculated by the Guggenheim method from the rising portion of the curves are also given in Table III.

Reaction of 2,4-Pentanedione with Mn^{3+}

A spectrophotometric record of the reaction of 2,4-pentanedione with Mn^{3+} ions in a solution of sulphuric acid is shown in Fig. 7. Curve 4. corresponds to concentration changes of the enol form and its rise is due to the reestablishing of the keto-enol equilibrium. The decreasing absorbancy at $18\,000 \text{ cm}^{-1}$ corresponds to the decreasing concentration of Mn^{3+} ions, which absorb also at $29\,000 \text{ cm}^{-1}$. When the changes of absorbancy at $29\,000 \text{ cm}^{-1}$ (curve 1) are corrected for the concentration changes of Mn^{3+} ions determined from curve 2, the concentration changes of the intermediate product are obtained (curve 3). Its maximum concentration depends on the initial

concentrations of Mn^{3+} , 2,4-pentanedione, and Mn^{2+} ions; and its spectrum determined by the flow-through method is shown in Fig. 1.

When the course of the oscillation reaction is followed at different wave numbers from 25 to $31 \cdot 10^3 \text{ cm}^{-1}$, other conditions being maintained constant, the character of the oscillation curve does not change, only the amplitude of the doubled oscillations increases. From the first couple of oscillations, the amplitude of the second oscillation (A_2) is determined as the difference between the absorbancies of the second maximum and first minimum on the oscillation curve (Fig. 3, curve 1). At the given wave numbers, the ratio of the absorbancy of the intermediate product (Fig. 1, curve 3) to the amplitude of the second oscillation A_2 is constant within the range of experimental errors (Table IV).

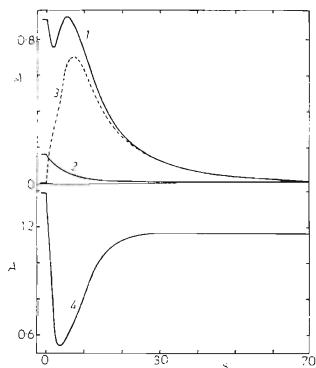


FIG. 7

Spectrophotometric record of reaction of 2,4-pentanedione with Mn^{3+} ions. Initial solution composition $5 \cdot 10^{-4} \text{ M-Mn}^{3+}$, $4 \cdot 10^{-4} \text{ M-Mn}^{2+}$, $1 \cdot 10^{-3} \text{ M-2,4-pentanedione}$, $1.5 \text{ M-H}_2\text{SO}_4$; 20°C . 1 $\tilde{\nu} = 29\,000 \text{ cm}^{-1}$, 50 mm cuvette (Mn^{3+} and intermediate product); 2 $\tilde{\nu} = 18\,000 \text{ cm}^{-1}$, 50 mm cuvette (Mn^{3+}); 3 curve for the intermediate product derived from curves 1 and 2; 4 $\tilde{\nu} = 36\,000 \text{ cm}^{-1}$, 10 mm cuvette (enol form)

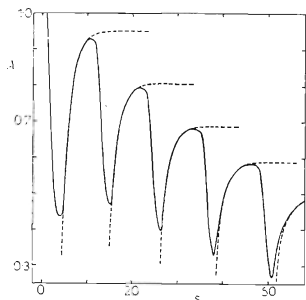


FIG. 8

Oscillation curve for enol form of 2,4-pentanedione compared with enolization curves; $\tilde{\nu} = 36\,000 \text{ cm}^{-1}$, 30°C , 10 mm cuvette. a Oscillation reaction, $1.6 \cdot 10^{-3} \text{ M-2,4-pentanedione}$, $8 \cdot 10^{-4} \text{ M-Mn}^{2+}$, 0.03 M-BrO_3^- , $1.5 \text{ M-H}_2\text{SO}_4$ (solid line); b restoration of the keto-enol equilibrium (dashed curves)

Dependence of Oscillation Reaction on Concentration of H₂SO₄ and Temperature

The dependence of the rate constant on the temperature and initial concentration of Mn²⁺ ions (Table II) was determined from the rising portion of the oscillations of the enol form by the Guggenheim's method. The curves of reestablishment of the keto-enol equilibrium were compared with the oscillation curve of the enol form (Fig. 8). The rising portion of the oscillations corresponds to the reestablishment of the mentioned equilibrium; the enol form concentration increases almost up to its equilibrium values. The amplitude of the oscillations of the enol form decreases with rising temperature while their number increases (Fig. 9). The temperature dependence of the reciprocal value of the period of the first oscillation gives an apparent activation enthalpy $\Delta H_{\text{osc}}^{\ddagger} = 66 \text{ kJ/mol}$. A decrease of the concentration of H₂SO₄ causes the oxidation of 2,4-pentanedione to become appreciably slower; this effect can be compensated for by increasing the initial concentrations of Mn²⁺ and BrO₃⁻ ions. (The rate constants at various concentrations of H₂SO₄, determined analogously to those in Table II, are given in Table I.)

DISCUSSION

It follows from our results that besides Mn³⁺ and Br⁻ ions, also the concentrations of the enol form and of the intermediate product, probably an intermediary [Mn(III)-enol] complex, oscillate in the studied system. The oscillations of the enol form of the substrate can be attributed to the fact that Mn³⁺ and bromine react preferentially with the enol form. When their concentration decreases, the keto-enol equilibrium is reestablished by enolization of the keto form; this corresponds to the increase of the enol form concentration.

After adding bromine to the substrate, bromination of the enol form proceeds rapidly ($k_{\text{Br}} \approx 10^6 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$, ref.¹⁷). Since the enolization rate constant is by more than six orders of magnitude lower, the enol form concentration drops to zero, the rate of bromination being then given by the rate of enolization of the keto form. After exhaustion of bromine, the tautomeric equilibrium is restored. The rate constant determined from the rising portion of the curves (Table III) is in good agreement with the rate constant for keto-enol equilibration ($k_{\text{e,sp}} = 0.374 \text{ s}^{-1}$). The time interval of bromination of the substrate, t_{Br} , depends on the initial concentration of bromine. The agreement between the measured and calculated (Eq. (2)) values of t_{Br} is in support of the assumed bromination mechanism (Table III). At higher initial bromine concentrations, bromination proceeds to the second stage, hence the experimental times are shorter than calculated. If the added bromine is equivalent to the equilibrium content of the enol form, the time dependence of the latter represents a single period of the oscillation.

Mn³⁺ ions also react with the enol form of 2,4-pentanedione. At an excess of the

TABLE III

Dependence of bromination kinetics of 2,4-pentenedione on initial bromine concentration. $8 \cdot 10^{-4}$ M-2,4-pentenedione, 20°C ; k_G^{Br} is the experimental rate constant determined by Guggenheim's method from the rising portion of the curve of the enol form, $t_{\text{Br}}^{\text{exp}}$ is the measured time of bromination, $t_{\text{Br}}^{\text{cor}}$ is that calculated from (2)

$[\text{Br}]_0 \cdot 10^4$ mol dm^{-3}	k_G^{Br} s^{-1}	$t_{\text{Br}}^{\text{exp}}$ s	$t_{\text{Br}}^{\text{cor}}$ s
1.8	0.39	1.9	1.9
3.6	0.38	8.2	8.1
5.4	0.42	16.7	16.8
7.2	0.44	27.6	32.1

TABLE IV

Dependence of absorbancy A of the intermediate product of the reaction of 2,4-pentenedione with Mn^{3+} and of the oscillation amplitude on the wave number (see text); $A/A_2 = 0.79 \pm 0.07$. Initial concentrations as in Fig. 3

$\tilde{\nu} \cdot 10^{-3}, \text{cm}^{-1}$	25	29	30	31
A	0.013	0.112	0.182	0.185
A_2	0.015	0.143	0.240	0.243

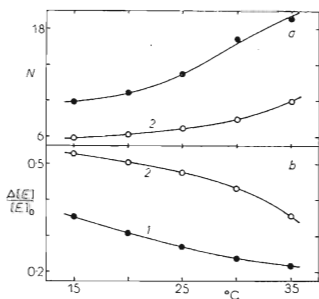
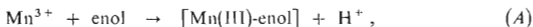


FIG. 9

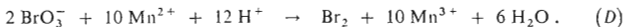
Dependences of a) total number of oscillations N and b) amplitude of the first oscillation $\Delta[E]/[E]_0$ on temperature; $1.6 \cdot 10^{-3}$ M pentanedione, $0.03\text{M} \cdot \text{BrO}_3^-$, $1.5\text{M} \cdot \text{H}_2\text{SO}_4$. Initial Mn^{2+} concentration: 1 $5 \cdot 10^{-4}$; 2 $8 \cdot 10^{-4}$ mol/dm³. Same symbols as in Fig. 4

substrate, when the concentration of Mn^{3+} ions drops to zero, the tautomeric equilibrium is restored, which corresponds to one oscillation of the enol form. The maximum at $29\,000\text{ cm}^{-1}$ on the spectrophotometric record of the reaction suggests the formation of an intermediate product, whose spectrum in the visible region was determined by the flow-through method. We have to deal probably with a $[\text{Mn(III)-enol}]$ complex formed in the first reaction step (A). In the subsequent step (B), an intramolecular redox reaction, it decomposes to Mn^{2+} and a radical of the enol form, which reacts with another Mn^{3+} ion¹⁸:

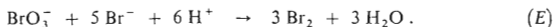


The dependence of the intermediate product formation (Fig. 7, curve 3) on the initial Mn^{2+} concentration suggests that the back reaction in step (B) probably plays a role; its kinetics and mechanism form the subject of our subsequent work.

Based on the F.K.N. mechanism of the Belousov-Zhabotinskii reaction with malonic acid¹⁹ and on our experimental results (related to the reactions of 2,4-pentanedione with Mn^{3+} and bromine and to the character of its oscillation reaction), we can assume the following mechanism of the oscillation reaction with 2,4-pentanedione. Every oscillation of the enol form can be divided into two phases, namely the decrease and the increase of its concentration. The first one involves the reaction of Mn^{2+} with BrO_3^- ions



The formed bromine and Mn^{3+} ions react rapidly with the enol form of the substrate causing its depletion. The reaction of Br_2 with the enol form leads to Br^- ions, which inhibit the oxidation of Mn^{2+} with bromate, step (D), since a concurrent reaction starts to proceed



Owing to reactions (A)–(C), the concentration of Mn^{3+} ions decreases. In the second phase, reaction (D) is inhibited, the production of Mn^{3+} and Br_2 is hindered and the keto-enol equilibrium restores. A comparison of the rate constants evaluated from the rising portion of the oscillations of the enol form, k_G , with those for the keto-enol equilibration, k_{exp} , at various temperatures (Table II) and concentrations of sul-

phuric acid (Table I) substantiates that the rising portion of the enol form oscillations corresponds to the enolization reaction under the given conditions.

Since the rate of formation of the intermediary [Mn(III)-enol] complex is higher than that of its decomposition and the Mn^{3+} concentration oscillates, the concentration of the complex shows oscillations with a phase shift against those of Mn^{3+} . The superposition of both these oscillations is manifested by double oscillations in the range of wave numbers from 25 to $31 \cdot 10^3 \text{ cm}^{-1}$. The second one of the oscillation couple corresponds to the mentioned complex, as follows from a comparison of the absorption curve of the intermediate product (obtained by the flow-through method) with the oscillation amplitude in the mentioned range of wave numbers (Table IV).

During the oscillation reaction, the concentration of 2,4-pentanedione decreases owing to bromination and oxidation with Mn^{3+} ions. When the concentration of the substrate and its monobromo derivative drops to zero, the concentration of Br^- ions decreases by reaction (E), hence they cease to inhibit reaction (D). The concentration of Mn^{3+} increases and is maintained constant by the bromate. The dibromo derivative of the substrate is oxidized by Mn^{3+} ions to give bromine, which accumulates in the solution. Its evolution rate depends on the concentration of the brominated substrate, therefore it is governed approximately by a first-order kinetics. The total evolved bromine concentration is proportional to the initial substrate concentration.

At a higher initial concentration of the substrate, that of the keto form is also higher and so is the rate of enolization resulting in a smaller amplitude of oscillations of the enol form. The amplitude of the oscillations of Mn^{3+} also decreases, since its reduction rate increases (reactions (A)–(C)). However, the rate of formation of the intermediary complex [Mn(III)-enol] and its concentration increase. Oxidation of the brominated substrate, whose concentration increases, results in a higher production of Br^- ions, whereby the oscillations are damped until they disappear and the reaction proceeds further monotonously.

The amplitude of the oscillations of Mn^{3+} depends on the ratio of the rates of the bidirectional reactions (A)–(D). When the initial 2,4-pentanedione concentration is relatively low and equal approximately to the two-fold analytical concentration of Mn, the equilibrium enol form concentration is close to the maximum Mn^{3+} concentration (*i.e.*, about 20% of the analytical one). Under these conditions, the substrate concentration decreases rapidly during the oscillation reaction, whereby the reduction of Mn^{3+} to Mn^{2+} (A)–(C) is slowed down and the amplitude of the oscillations of Mn^{3+} increases.

The apparent activation enthalpy, ΔH_{osc}^\ddagger , calculated from the temperature dependence of the oscillations of the enol form, is much higher than that for enolization, ΔH_E^\ddagger , and the experimental value, ΔH_{exp}^\ddagger , determined from the rate constant for the keto-enol equilibration, k_{exp} , although every oscillation is due mainly to enolization. This disagreement is due to the fact that the oscillation amplitude of the enol form

decreases with rising temperature and their period decreases still more. Hence, the value of $\Delta H_{\text{osc}}^{\ddagger}$ characterizes only the temperature dependence of the oscillation period and it cannot be regarded as the activation enthalpy of a certain reaction step.

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