Influence of temperature on oscillating reaction with lactic, tartaric, and oxalic acid

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Lactic acid generates chemical oscillations in the Belousov—Zhabotinskii reaction if the solution is bubbled through with nitrogen. The frequency of oscillations f of heterogeneous oscillating reactions depends on temperature. The linear relationship between ln $\{f\}$ and $1/T$ was used for determining activation energies of the oscillating reactions of the Belousov—Zhabotinskii type with substrates which cannot undergo bromination, *i.e.* lactic, tartaric, and oxalic acid at equal initial concentrations of reactants.

Молочная кислота вызывает химические осцилляции в реакции Белоусова—Жаботинского, если через раствор пробулькивается азот. Частота осцилляций гетерогенных осцилляционных реакций зависит от температуры. Исходя из линейной зависимости ln{f} от $1/T$ были вычислены энергии активации осцилляционных реакций типа Белоусова—Жаботинского с небромируемыми субстратами и с молочной, винной и щавелевой кислотами при одинаковых исходных концентрациях реагентов.

In the study of oscillating reactions we have paid attention to substrates which cannot be brominated. In contrast to the substrates in the classical Belousov—Zhabotinskii reaction (BZ), these substrates do not give any brominated derivatives the reaction of which with oxidized forms of catalyst produces the Br$^-$ ions which are regarded as key intermediate in oscillating reaction [1]. A system with substrate which cannot undergo bromination exhibits oscillations only if the arising bromine which is an inhibitor of oscillations is removed by a stream of inert gas. The heterogeneous oscillating reaction of the BZ type with oxalic acid as substrate was revealed by *Noszticzius* and *Bódiss* [2] who considered it to be an oscillating reaction which was not controlled by bromide [3].

The oscillating systems of the BZ type with substrates which cannot be brominated, *i.e.* the hypophosphite ions [4], oxalic [5], tartaric [6], and mandelic [7] acid were described in preceding papers. In this paper, we describe oscillations in the system with further substrate which does not undergo bromination, *i.e.* lactic acid that plays an important part in the metabolism of living systems and is a product of anaerobic glycolysis of animals.

The oscillation period of the classical BZ reaction (BrO_3^-, H_2SO_4, malonic acid, catalyst) as a function of temperature was studied by several authors [8—11] who calculated the activation energy of oscillating reaction by means of the Arrhenius equation. For heterogeneous oscillating reactions with substrates which cannot be brominated, the temperature dependence of the period or frequency of oscillations has not been measured. The activation energies of three heterogeneous oscillating reactions of the BZ type with lactic, tartaric, and oxalic acid serving for substrate are evaluated and compared for equal initial concentrations of reactants in this paper.

Experimental

The used solutions were freshly prepared by dissolving anal. grade chemicals in redistilled water. Lactic acid was distilled at the pressure of 1600 Pa and its purity was checked by measuring the index of refraction. The solution of the manganese(III) ions was prepared by reduction of permanganate by excess manganese(II) sulfate in 5 M-H_2SO_4.

A bromide ion-selective electrode CRYTUR, Type 35—17, was used. It was dipped in the reaction solution which was constantly bubbled through by nitrogen used in electric bulb industry. A 1 M-mercury sulfate electrode (MSE) was used as reference electrode. The electromotoric force of this cell was measured by a polarograph OH-105 (Radelkis, Budapest) which was connected as a millivoltmeter.

When the oscillations of bromine were measured, the oscillating reaction took place in a thermostated glass reaction vessel from which the volatile products were transported by bubbling nitrogen into a Kalousek polarographic vessel. The only polarographically active substance, *i.e.* bromine was continuously determined in the Kalousek vessel in 1.5 M-H_2SO_4 at the potential of -0.6 V against 1 M-MSE. A constant flow of nitrogen was kept by a laboratory flow-meter of the type TG 400. The details concerning the experimental procedure are described in paper [5]. The rate constant of the oxidation of lactic acid by bromine was determined from the time dependence of the polarographic limiting current of bromine at the potential of -0.6 V against 1 M-MSE. The oxidation of lactic acid by the Mn(III) ions was investigated at the potential of -0.2 V against 1 M-MSE which corresponded to the limiting diffusion current of Mn(III) in 1.5 M-H_2SO_4. The kinetics as well as oscillations was investigated with a polarograph OH-105 (Radelkis, Budapest). The temperature of the reaction system was held constant accurate to ± 0.1 K by the use of an ultrathermostat U 15C (Medingen) and an immersion cooler of liquids LPCH-2. The temperature varied from 5 °C to 25 °C.

Results

Provided the solution was bubbled through by nitrogen with constant flow rate, we observed periodic formation of bromine, periodic changes in concentrations of Mn(II) and Mn(III), and periodic changes in potential of the bromide ion-selective electrode during oxidation of lactic acid by bromate in the medium of sulfuric acid and in the presence of the Mn(II) ions as catalyst. A typical course of the oscillating reaction with lactic acid is represented in Fig. 1. Curve *a* represents the oscillations of bromine. The maxima in
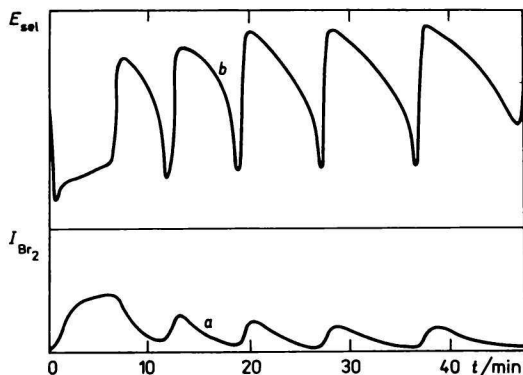

Fig. 1. Course of oscillations with lactic acid.
a) Time dependence of limiting polarographic current of bromine; b) time dependence of potential of the bromide ion-selective electrode.
8×10^{-3} M-KBrO₃, 0.2 M-lactic acid, 3×10^{-3} M-MnSO₄, 1.5 M-H₂SO₄, 20 °C, rate of N₂ flow 600 cm³ min⁻¹, 10 cm³ of reaction solution.

bromine concentration arise owing to continuous transport of the bromine formed in the reaction vessel into the Kalousek polarographic vessel. For the nitrogen flow rate of $600 \text{ cm}^3 \text{ min}^{-1}$, the maximum of bromine concentration in the reaction vessel manifests itself by a maximum in the Kalousek vessel with time delay of 40 s. The oscillations in the Mn(II)—Mn(III) concentration were visually observed in the reaction vessel. The characteristic rosy colour belonging to Mn(III) was accompanied by increase in bromine concentration in the Kalousek vessel. Curve *b* in Fig. 1 represents changes in potential of the bromide ion-selective electrode dipped into solution in the reaction vessel. Its course shows clearly the induction period *IP* measured from the start of reaction up to the time moment when the system begins to oscillate as well as the frequency of oscillations *f* (reciprocal value of the period of oscillations). Both the induction period and frequency are well reproducible quantities under given conditions. For instance, *IP* for the system in Fig. 1*a* was 425 s and the frequency calculated from the second period was $2.38 \times 10^{-3} \text{ s}^{-1}$. For comparison, *IP* determined from the time dependence of the potential measured with a bromide ion-selective electrode was 435 s and the frequency of oscillations was $2.38 \times 10^{-3} \text{ s}^{-1}$. These both quantities are sensitive to temperature. The induction period decreases with temperature

and the frequency increases with temperature. The plot $\ln \{f\}$ against $1/T$ is a straight line and its slope was used to calculate the activation energy E_t of the oscillating reaction by means of the Arrhenius equation. Besides the temperature dependence of the heterogeneous oscillating reaction with lactic acid, we measured the temperature dependences of the heterogeneous oscillating reactions with tartaric and oxalic acid and evaluated their activation energies for three different flow rates of nitrogen. As the activation energy is a function of initial concentration of the substances constituting an oscillating system [11], we sought for the conditions under which the systems containing all three substrates, *i.e.* lactic, tartaric, and oxalic acid oscillate at equal initial concentrations of reactants. The initial conditions were as follows: 8×10^{-3} M-BrO$_3^-$, 8×10^{-2} M-substrate, 3×10^{-3} M-Mn(II), 1.5 M-H$_2$SO$_4$, flow rates of nitrogen 400 cm^3 min^{-1}, 600 cm^3 min^{-1}, and 833 cm^3 min^{-1} in 10 cm^3 of the reaction solution. The values of activation energy are given in Table 1.

Table 1

Activation energies E_t for substrates which cannot be brominated and different rates of nitrogen flow
8×10^{-3} M-BrO$_3^-$, 8×10^{-2} M-substrate, 3×10^{-3} M-Mn(II), 1.5 M-H$_2$SO$_4$

Substrate	$E_t/(\text{kJ mol}^{-1})$		
	Rate of N$_2$ flow/(cm^3 min^{-1})		
	400	600	833
Lactic acid	48	41	30
Tartaric acid	41	40	42
Oxalic acid	49	42	31

The redox reactions of bromine with lactic acid and Mn(III) ions with lactic acid were investigated in the presence of excess lactic acid (8×10^{-2} M-lactic acid, 1.5 M-H$_2$SO$_4$, 20 °C). The rate constants of the pseudo-first order k_{obs} were evaluated from linear plot $\ln I_0/I = f(t)$. The rate constant of the reaction of bromine with lactic acid was $k_{obs} = 2 \times 10^{-3}$ s^{-1} while the rate constant of the reaction of Mn(III) with lactic acid was $k_{obs} \geqq 7 \times 10^{-2}$ s^{-1}.

Discussion

In the preceding paper, we alleged the conditions under which oscillations in the systems with substrates which cannot be brominated may be observed [7]. Like other substrates which do not undergo bromination, lactic acid is also oxidized by the bromate ions very slowly. However, it is valid for the condition that the arising bromine is removed from the reaction system by sufficient flow of an inert gas. If the reaction proceeds under homogeneous conditions (without bubbling), it has autocatalytic character. It is remarkable that the oxidation of all hitherto described

substrates of oscillating reactions which cannot be brominated by the bromate ions is autocatalytic under homogeneous conditions. According to *Noszticzius* [12], just these reactions are producers of bromous acid $HBrO_2$ and hypobromous acid $HBrO$ which are essential intermediates in the four-parameter Lotka—Volterr scheme. Lactic acid reacts with bromine slowly ($k_{obs} = 2 \times 10^{-3}$ s^{-1}, 8×10^{-2} M-lactic acid, 1.5 M-H_2SO_4, 20 °C) while its reaction with Mn(III) is relatively rapid ($k_{obs} \geqq 7 \times 10^{-2}$ s^{-1}, 8×10^{-2} M-lactic acid, 1.5 M-H_2SO_4, 20 °C). The continuous removal of bromine is a necessary condition for producing oscillations of catalyst and bromine in the investigated systems within a given concentration range of reactants. By using the smallest flow rate of nitrogen, *i.e.* 400 cm^3 min^{-1}, bromine was removed from the reaction vessel at 13 °C with constant half-life of 49 s, which corresponded to the first-order rate constant $k = 1.4 \times 10^{-2}$ s^{-1} while half-life of 23 s was attained by the highest flow rate of nitrogen 833 cm^3 min^{-1} at 25 °C, which corresponded to $k = 3 \times 10^{-2}$ s^{-1}. In a continuously stirred through-flow reactor (CSTR) oscillations were observed even in the system which consisted only of the BrO_3^- ions, Br^- ions, and catalyst [13].

If one of the reactions in the investigated oscillation cycle is considerably more sensitive to temperature change, then the variation of oscillation frequency with temperature may be used for identifying such reaction. According to *Körös* [8], the activation energy of oscillation frequency with a classical BZ substrate is independent of the used catalyst and equals $E_t = 67$—69 kJ mol^{-1}. *Blandamer* [9] attributes the measured value $E_t = 70$ kJ mol^{-1} to the step in which the bromate ions react with the bromide ones to give $HBrO_2$. According to *Edelson* [14], the frequency of oscillations is predominantly affected by the reactions in which the enol form of malonic acid arises. This species is subsequently brominated to give the Br^- ions.

The activation energies of the oscillating reactions with substrates which do not undergo bromination (Table 1) are evidently lower than activation energies in a classical BZ system. As for substrates which cannot be brominated, some reactions in the classical FKN mechanism of the BZ reaction may be excluded, but the effect of nitrogen bubbling through the reaction solution arrives. However, the physical removal of bromine affects not only its concentration but also the concentration of the Br^- ions and $HOBr$ which are in mobile equilibrium with it.

In order to ascertain the influence of temperature on the rate of bromine removal, the temperature dependence of the rate of bromine removal from the reaction vessel was measured for varying flow rates of nitrogen. The Arrhenius equation was used for evaluating the value of activation energy (21 kJ mol^{-1}) which was independent of the rate of nitrogen flow in the range 400—600 cm^3 min^{-1}. It is a value characteristic of the processes controlled by diffusion. Therefore it seems improbable that the only factor determining the activation energy is a physical process. We found the value $E_t = 41$ kJ mol^{-1} for all three acids and the rate of nitrogen flow of 600 cm^3 min^{-1}. This value approximates

to the value $E_v = 42$ kJ mol^{-1} which is given by *Yoshikawa* [11] for spatial oscillations in the classical BZ system. This value respects the diffusion as well as the rate-determining autocatalytic reaction of the bromate ions with bromous acid.

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