Source of the bromide ions in the oscillation reaction of the Belousov—Zhabotinskii type with D-glucose

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The redox reaction between the bromate ions and D-glucose is autocatalytic in homogeneous medium. Provided the bubbling with nitrogen is sufficient, it is a first-order reaction with respect to both reactants and $k = 2.02 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} in 1 M-H$_2$SO$_4$ at 25 °C. For an aqueous solution of bromine and D-glucose the oxidizing particle is the bromine molecule and the two-electron reaction pathway through HOBr is relatively unimportant for production of the Br$^-$ ions. The reaction of Br$_2$ with D-glucose is light-sensitive and in dark it is a first-order reaction with respect to both reactants while it holds $k = 5.57 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} in 1 M-H$_2$SO$_4$ at 25 °C. There are indications that the bromine atoms are precursor of the bromide ions in the investigated system.

Реакция восстановления бромат-ионов D-глюкозой является автокаталитической в гомогенной среде. При достаточном продувании азотом она проходит по первому порядку по обоим реагентам, причем $k = 2,02 \cdot 10^{-3}$ дм^3 моль$^{-1}$ с$^{-1}$ в 1 M-H$_2$SO$_4$ при 25 °C. В водном растворе брома и D-глюкозы окисляющей частицей является бром, а двухэлектронный реакционный путь через HOBr не представляет особой важности для образования ионов Br$^-$. Реакция Br$_2$ с D-глюкозой чувствительна к свету и в темноте проходит по первому порядку по обоим реагентам с $k = 5,57 \cdot 10^{-4}$ дм^3 моль$^{-1}$ с$^{-1}$ в 1 M-H$_2$SO$_4$ при 25 °C. Сделан вывод, что предшественником ионов Br$^-$ в изучаемой системе являются атомы брома.

Saccharides can be used as substrates of oscillation reactions of the Belousov—Zhabotinskii (BZ) type under conditions of continuous removal of the arising bromine by nitrogen stream [1] or by adding a substance which can be easily brominated (acetone) [2] or in an isothermal closed system [3]. Glucose belongs among the substrates which cannot be brominated and for this reason it is not possible to apply the original Field—Körös—Noyes (FKN) mechanism to it [4] because this mechanism assumes the formation of the Br$^-$ ions by oxidation of the brominated derivative of substrate by the oxidized form of

catalyst. The later Field model [5] explains the oscillations in the presence of the substrates which are not able to be brominated on the assumption that the decrease in bromine concentration during oscillation reaction is assured by physical or chemical means or in the continuous stirred tank reactor (CSTR). In the original FKN as well as Field model the bromide ions are regarded as controlling intermediate the concentration change of which is responsible for the change-over of the sequence of the nonradical reactions involving oxidation of the Br^- ions by the BrO_3^- ions and of the sequence of the radical reactions involving oxidation of the Ce(III) or Mn(II) ions by the BrO_3^- ions.

In the revised [6] as well as extended [7] Oregonator [8] it is assumed that the Br^- ions originate in the reaction of HOBr with substrates. In addition, the reversible hydrolysis of bromine is also taken into account in the Field model [5]. The experimental results suggest [9] that this assumption may be accepted for the oscillating system containing other substrate which cannot get brominated, *i.e.* oxalic acid [10, 11]. The numerical simulation of oscillations in the BZ system containing oxalic acid can be accomplished if it is assumed that the Br^- ions are formed at appropriate values of the parameter of bifurcation such as the rate constant describing the rate of physical removal of bromine [12—14]. However, if the value of this parameter is equal to zero and the system is batch and closed, no model hitherto published is able to explain oscillations in the presence of a substrate which does not undergo bromination.

In the completely inorganic oscillating system of the BZ type containing the hypophosphite ions [15] the reaction between bromine and substrate was identified as a reaction in which the Br^- ions may originate [9] while the homogeneous redox reaction of the BrO_3^- ions with NaH_2PO_2 exhibits autocatalytic character [9, 16]. However, the conditions under which this inorganic substrate would produce oscillations in a homogeneous closed system without a mechanism removing bromine have not been found yet. In this case, the bubbling with inert gas [17], addition of acetone [2] or CSTR [18] is necessary.

As recently shown by *Körös* and coworkers [19], even in the classical BZ reaction with malonic acid most of the Br^- ions come from the BrO_3^- ions and not from bromomalonic acid. The reaction pathway leading through HOBr to the Br^- ions is thus indicated again [20].

Therefore the problem in which reactions and with what rate the Br^- ions arise is of principal importance for studying the mechanism of oscillation reactions of the BZ type. From this point of view, the kinetics of oxidation of D-glucose by the bromate ions and bromine has been studied in the medium used for the BZ reaction, *i.e.* in $1 M-H_2SO_4$. Besides, the numerical values of the rate constants are necessary for the numerical simulation of the oscillation reaction with D-glucose.

Experimental

All solutions were prepared from anal. grade chemicals and redistilled water.

The kinetics of oxidation of D-glucose by the BrO_3^- ions was investigated polarographically. The time dependence of the limiting diffusion current of the BrO_3^- ions was recorded at the constant potential of -1 V against 1 M mercurous sulfate electrode (MSE). The dependence of the limiting diffusion current of the BrO_3^- ions on their concentration was linear while D-glucose was polarographically inactive at the potential used. The reaction took place in a Kalousek polarographic vessel equipped with thermostated jacket at (25 ± 0.1) °C. The nitrogen bubbling (with the rate 0.6 dm^3 min^{-1}) was used for removing the dissolved atmospheric oxygen and in some cases for reducing physically the concentration of bromine in reaction. In our experimental arrangement it corresponded to "the rate constant" of 2.3×10^{-2} s^{-1}. For reading the precise values of the limiting diffusion current of the BrO_3^- ions, it was necessary to stop the stream of nitrogen for 4—5 s approximately every 10 min. A polarograph Radelkis OH-105 was used.

The kinetics of oxidation of D-glucose by aqueous solution of bromine was also investigated polarographically. In this case the time dependence of the limiting diffusion current of Br_2 was investigated at the constant potential of -1 V against 1 M-MSE at 25 °C. Nitrogen was used only for removing the air oxygen from solution before the reaction.

For investigating the kinetics of oxidation of D-glucose by the BrO_3^- ions under constant nitrogen bubbling and the kinetics of oxidation of D-glucose by bromine we used sufficient excess of D-glucose (30—500-fold) so that we could evaluate the rate constants from the rate equation of the pseudofirst-order reaction $\ln (I_0/I) = k_{exp} t$ where I_0 is the polarographic limiting diffusion current at the beginning of reaction and I in the time moment t.

Both these reactions were also investigated spectrophotometrically on an instrument Specord UV VIS at the wavelength of 400 nm corresponding to the absorption maximum of Br_2 ($\varepsilon = 16.6$ m^2 mol^{-1}). The absorbance A of reaction solution was measured in thermostated 0.5—2 cm cells (BrO_3^- + D-glucose) or in 5 cm cells (Br_2 + D-glucose) at (25 ± 0.1) °C. The reaction of BrO_3^- ions with D-glucose without nitrogen bubbling proceeded autocatalytically under homogeneous conditions. The rate constants of the reaction of Br_2 with D-glucose were evaluated from the relationship $\ln (A_0/A) = k_{exp} t$ similarly as in polarographic investigations. The rate constants of the reaction of bromine in aqueous solution with D-glucose obtained spectrophotometrically (mean error ± 5 %) were in a good agreement with the values obtained polarographically in a blackened reaction vessel (mean error ± 7 %).

Results

Oxidation of D-glucose by bromate ions

In the presence of excess D-glucose the Br^- ions are the final reduction product while Br_2 is an intermediate. It has been suggested by spectrophotomet-

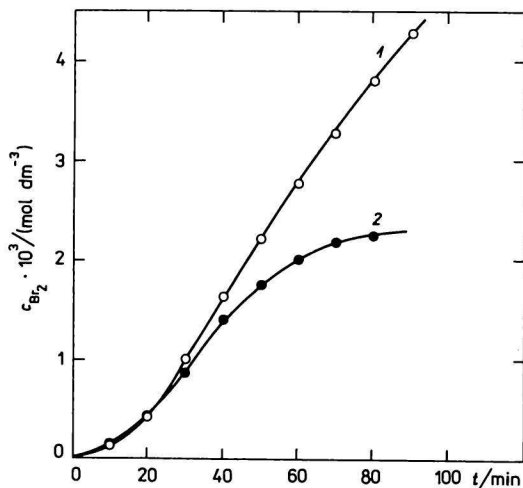Fig. 1. Formation of bromine in the reaction (1 M-H_2SO_4, 25 °C):
1. 0.5 M-BrO_3^- + 0.005 M D-glucose,
2. 0.005 M-BrO_3^- + 0.3 M D-glucose.

ric investigations of the Br_2 concentration and confirmed by polarographic investigations of the BrO_3^- concentration that the oxidation of D-glucose proceeds in homogeneous medium autocatalytically (Fig. 1). The typical sigmoid curves were obtained in either case. However, if the flow of nitrogen is sufficient, the course of the reaction obeys the kinetics of the first-order reaction with respect to concentration of the BrO_3^- ions (Fig. 2). The observed first-order rate constants were linearly dependent on D-glucose concentration. For this reason, the rate equation may be expressed in the following form

$$-\frac{d[BrO_3^-]}{dt} = k\,[BrO_3^-]\,[\text{D-glucose}] \tag{1}$$

where $k = 2.02 \times 10^{-3}$ $dm^3\,mol^{-1}\,s^{-1}$ in 1 M-H_2SO_4 at 25 °C.

The suppression of autocatalytic character of the reaction by nitrogen means that either the component giving rise to autocatalyst has been removed or the concentration of autocatalyst has decreased under the lowest value influencing the rate of reduction of the BrO_3^- ions. Nitrogen is able to remove only Br_2 from the reaction solution, "the rate constant" being 2.3×10^{-2} s^{-1}. But the hydrolytic equilibrium is rapidly established in aqueous solution

$$Br_2 + H_2O \overset{K_h}{\rightleftharpoons} HOBr + Br^- + H^+ \tag{A}$$

where $K_h = 1.37 \times 10^{-8}$ $mol^2\,dm^{-6}$, $k_h = 110\,s^{-1}$ and $k_{-h} = 8 \times 10^9$ $dm^6\,mol^{-2}\,s^{-1}$ [21]. The later values $K_h = 6.66 \times 10^{-10}$ $mol^2\,dm^{-6}$, $k_h = 2\,s^{-1}$ and $k_{-h} = 3 \times 10^9$ $dm^6\,mol^{-2}\,s^{-1}$ for 1 M-H_2SO_4 do not change the qualitative aspect of the problem [22]. Besides, they were criticized in paper [23].
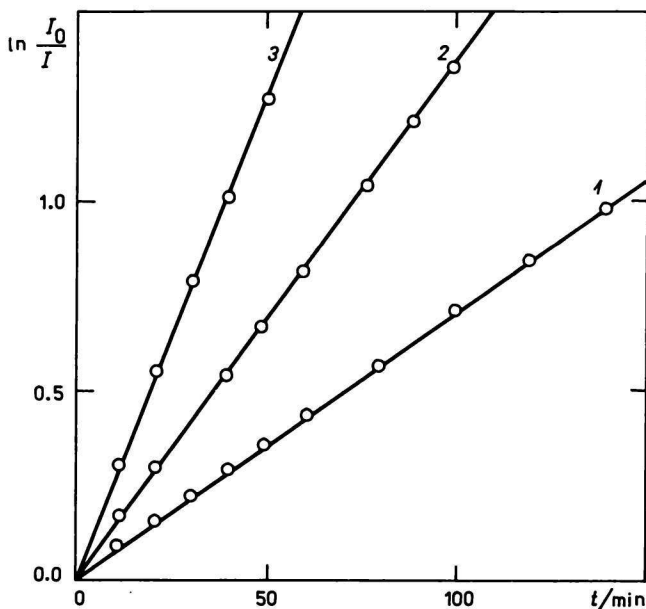
Fig. 2. Evidence of a first-order reaction with respect to the BrO_3^- ions (10^{-3} M-BrO_3^-, 1 M-H_2SO_4, flow rate of nitrogen 600 cm^3 min^{-1}, 25 °C) for *1.* 0.05 M D-glucose, *2.* 0.1 M D-glucose, *3.* 0.2 M D-glucose.

Oxidation of D-glucose by aqueous solution of bromine

The decrease in Br_2 concentration in the course of the reaction of aqueous bromine solution with D-glucose follows the kinetics of the first-order reaction in the whole investigated interval (3 halflives) if a sufficient excess of D-glucose is available. The Br^- ions are the final product of reduction. The reaction runs without any observable retardation by the arising Br^- ions which influence the instantaneous concentration of HOBr because of fast reaction (*A*). This fact itself indicates that HOBr is not the real oxidizing agent in the aqueous solution of bromine.

The rate constants óf the reaction of bromine with D-glucose in aqueous solution as well as the reaction order of this reaction with respect to D-glucose significantly depend on the condition whether the reaction takes place in dark or in light. The spectrophotometric investigation led to the first reaction order with respect to D-glucose and to the rate equation

$$-\frac{d[Br_2]}{dt} = k\,[Br_2]\,[\text{D-glucose}] \qquad (2)$$

where $k = 5.67 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$ in 1 M-H_2SO_4 at 25 °C.

The reaction order with respect to D-glucose obtained by polarographic investigation of concentration of Br_2 in a blackened Kalousek vessel was equal to 0.83 whereas it was equal to 0.65 if the experiments were carried out in light. That means for the 0.1—0.3 M solution of D-glucose that the rate constants of the first-order reaction observed in light were three or four times higher than those observed in dark.

The problem whether the Br^- ions are produced by bromine or HOBr may be elucidated by the experiments in which the initial concentration of HOBr is varied by means of a change in concentration of the H^+ or Br^- ions at a constant initial concentration of Br_2. Therefore the influence of the concentration of H^+ ions on the kinetics of oxidation of D-glucose by bromine in aqueous solution was investigated at constant ionic strength (2 mol dm^{-3}) in the medium NaClO$_4$—HClO$_4$. The increase in initial concentration of HClO$_4$ from 0.1 mol dm^{-3} to 2 mol dm^{-3} brings about a 4.5-fold decrease in initial equilibrium concentration of HOBr at $c(Br_2) = 10^{-3}$ mol dm^{-3} (the decrease due to hydrolysis is equal to 1.1 % at most). The change in initial concentration of HOBr from 1.12×10^{-5} to 2.62×10^{-6} mol dm^{-3} owing to the fast equilibrium reaction (A) did not have any perceivable influence on the rate constant (K_h according to [21]).

The results obtained by studying the influence of concentration of the Br^- ions on the rate constant of the reaction of bromine in aqueous solution with D-glucose at a constant concentration of the H^+ ions in the medium of 1 M-H_2SO_4 are still more convincing. The reaction remains of the pseudofirst order (Fig. 3). The decrease in initial equilibrium concentration of HOBr from 3.6×10^{-6} mol dm^{-3} (provided no Br^- ions were added and only the hydrolysis of 10^{-3} M solution of Br_2 produced them) to 1.3×10^{-8} mol dm^{-3} or to 9.62×10^{-9} mol dm^{-3} in the presence of 10^{-3} M, resp. 5×10^{-3} M solution of Br^- ions resulted in a change in rate constant reaching 3 % at maximum. Though the initial concentration of HOBr decreased 374 times, it had no significant influence on the rate of the reaction of aqueous solution of bromine with D-glucose in dark.

Discussion

The following reaction scheme is consistent with autocatalytic course of the oxidation of D-glucose by the BrO_3^- ions in homogeneous medium, its suppression by the effect of nitrogen bubbling and reaction orders
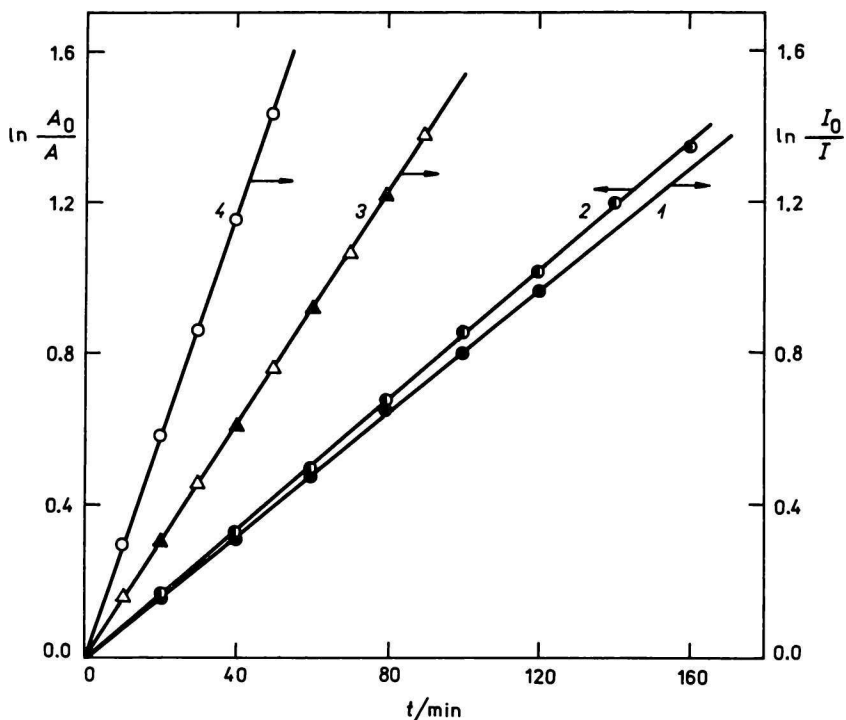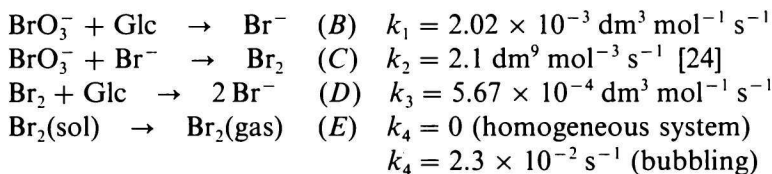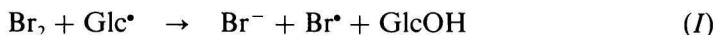
Fig. 3. Polarographic and spectrophotometric investigation of the reaction of Br_2 with D-glucose (1 M-H_2SO_4, 25 °C).
1. 2.25×10^{-3} M-Br_2 with 0.3 M D-glucose, polarographic, in dark; *2.* 2.25×10^{-3} M-Br_2 with 0.3 M D-glucose, spectrophotometric; *3.* 3×10^{-3} M-Br_2 with 0.5 M D-glucose ($\triangle$), addition of 10^{-3} M-Br^- ($\blacktriangle$), polarographic, in dark; *4.* like *3.* but in light.

$$
\begin{array}{llll}
BrO_3^- + Glc & \rightarrow & Br^- & (B) \quad k_1 = 2.02 \times 10^{-3} \ dm^3 \ mol^{-1} \ s^{-1} \\
BrO_3^- + Br^- & \rightarrow & Br_2 & (C) \quad k_2 = 2.1 \ dm^9 \ mol^{-3} \ s^{-1} \ [24] \\
Br_2 + Glc & \rightarrow & 2\,Br^- & (D) \quad k_3 = 5.67 \times 10^{-4} \ dm^3 \ mol^{-1} \ s^{-1} \\
Br_2(sol) & \rightarrow & Br_2(gas) & (E) \quad k_4 = 0 \ (\text{homogeneous system}) \\
& & & \qquad k_4 = 2.3 \times 10^{-2} \ s^{-1} \ (\text{bubbling})
\end{array}
$$

We may deduce from kinetic study of the reaction of bromine with D-glucose in aqueous solution as well as from the influence of concentration of the H^+ and Br^- ions on the rate constant of this reaction that the two-electron reaction pathway through HOBr is relatively unimportant for production of the Br^- ions. Its rate ought to be dependent on concentration of HOBr and D-glucose and should be only little influenced by the presence of radicals in the system. As for one-electron reactions, the rate of formation of the Br^- ions must be

sensitive to the presence of radicals. The influence of light on the rate of the reaction of Br_2 with D-glucose in aqueous solution is in line with a one-electron reaction pathway.

$$Br_2 \xrightarrow{h\nu} 2\,Br^\bullet \tag{F}$$

$$HOBr + Glc \rightarrow Br^\bullet + Glc^\bullet \tag{G}$$

$$Br^\bullet + Glc \rightarrow Br^- + Glc^\bullet \tag{H}$$

$$Br_2 + Glc^\bullet \rightarrow Br^- + Br^\bullet + GlcOH \tag{I}$$

$$HOBr + Glc^\bullet \rightarrow Br^\bullet + GlcOH \tag{J}$$

The atomic bromine the concentration of which increases by the effect of light affects the rate of formation of the Br^- ions through reaction (H). The one-electron radical reaction is also evidenced by the observation that the oxidation of D-glucose by bromine in aqueous solution is induced by the Mn(III) ions [1]. The Mn(III) ions are a one-electron agent and the formation of $Glc^\bullet$ from D-glucose is much faster than it is in the case of oxidation by the BrO_3^- ions or Br_2. These facts suggest that Br_2 oxidizes D-glucose much more rapidly if radicals arise from the reduction agent in other reaction and the atoms of bromine are the precursor of the Br^- ions in the investigated system. The role of the organic radical as the second controlling intermediate in the classical BZ reaction was recently pointed out by *Försterling* and *Noszticzius* [25].

The results of kinetic study of the oxidation of D-glucose by the BrO_3^- ions and bromine suggest that it does not suffice for a model of oscillation reactions of the BZ type proceeding in closed systems with substrates unable to undergo bromination to assume the formation of the Br^- ions only through the reaction of HOBr with substrate. Neither assumption of such a source of the Br^- ions in the closed oscillating system with oxalic acid without removal of bromine is in line with oscillating behaviour of the models published up to now. Still, the oscillations were observed experimentally [26].

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