THE BELOUSOV–ZHABOTINSKII OSCILLATORY REACTION INVOLVING SOME ORGANIC CHIRAL SUBSTRATES

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Oscillatory systems of the Belousov–Zhabotinskii (BZ) type were studied using the following substrates: D-gluconic and D-galactonic acids, their lactones, and D-glucose and D-galactose. The systems were either nitrogen purged or left undisturbed. It is suggested that during the induction period (IP), reactions occur giving rise to the active substrate in the BZ system which need not be identical with the organic substance with which the oscillatory system starts up. A special dependence of the IP on sulfuric acid concentration was measured, exhibiting a minimum and a maximum; the dependence on perchloric acid concentration displayed a minimum.
Key words: Chemical oscillations; BZ type bromate oscillators; Induction period.

The Belousov–Zhabotinskii (BZ) reaction, which is oxidation of malonic acid (MA) by bromate ions in aqueous sulfuric acid catalyzed by cerium(III) ions, is a classical bromate chemical oscillation[1,2]. The mechanism of the BZ reaction was elucidated in 1972 by Field, Körös, and Noyes and is referred to in the literature as the FKN mechanism[3]. Despite a vast volume of available experimental data, some problems of the BZ reaction have not yet been solved, particularly with respect to organic reactants and the role of organic intermediates in the chemical mechanism. Such reactions constitute Process *C* in the FKN mechanism. Organic substrates react with the oxidized form of the catalyst, *e.g.* manganese(III) ions, which, however, can be present in various kinetically active species. The coordination chemistry of manganese(III) in the BZ environment is highly complex and affects considerably the kinetics and stoichiometry of Process *C*. Many organic substances have been employed as substrates in the BZ reaction[4]. Some of them were readily brominable substrates where the mechanism is similar to that occurring with MA (ref.[5]), whereas some other substrates reacted in a different manner – those were bromo-hydrolysis-controlled (BHC) oscillators[6]. In such cases the excess bromine usually has to be removed from the system either physically[7,8] or chemically[9]. Other organic substrates are transition ones; these include, for instance, D-gluconic and D-galactonic acids and their lactones, D-glucose and D-galactose, which we found to be suitable BZ substrates. Oscillatory reactions with saccharides were our concern previously[10,11] and we demonstrated that oscillations can be generated either while physi-

cally removing Br_2 from the system or, in a closed system, without Br_2 removal, in dependence on the starting concentrations chosen. In BZ systems with some saccharides, Rastogi and Srivastava[12] trapped bromine chemically by using acetone. The BZ system with the simplest sugar, glyceraldehyde, has also been studied[13].

The oscillatory patterns with the above substrates are very similar. Apparently, the initial substrate transforms to the active substrate by oxidation-reduction reactions during the BZ process. For instance, bromine is known to act as oxidant in neutral or acid solutions, converting saccharides directly to aldonic lactones.

We paid particular attention to the effects of sulfuric and perchloric acids, present in very wide concentration ranges, on the oscillation parameters.

EXPERIMENTAL

All chemicals were of reagent grade purity (Merck, Chemprosa Lannach), and solutions were prepared using redistilled water. Fresh solutions were employed in all measurements.

The time dependences of the potential of a platinum redox electrode (5 mm × 8 mm, Radelkis) submerged in the reaction solution in a Kalousek vessel were recorded by using a Radelkis OH-105 polarograph in the potentiometric mode. A mercury sulfate electrode served as the reference electrode. The reaction solution was purged with nitrogen fed at a rate of 83 ml/min, as adjusted with a TG 400 laboratory flowmeter. The measurement temperature was 25 ± 0.1 °C. In the batch experiments (without the use of nitrogen) as well as in the experiments using nitrogen bubbling, the reactants (aqueous solutions) were added in the following order: H_2SO_4, $MnSO_4$, substrate, $NaBrO_3$. The starting concentrations were as follows: $MnSO_4$ 5 mmol l^{-1}, substrate 50 mmol l^{-1}, $NaBrO_3$ 100 mmol l^{-1}; the concentrations of sulfuric or perchloric acid were variable. Oxygen, which inhibits the oscillation systems investigated, was removed from the batch systems by 10–15 min nitrogen purging before addition of the last component.

The parameters measured included the oscillation parameters, induction period, and period of oscillations. The induction period (IP) is the time t_i elapsed from the reactant mixing to the start of oscillations; the period of oscillations is the time between two adjacent oscillation peaks (the average of the first 3 oscillations was calculated). Each measurement was repeated 3 to 5 times, and the standard deviation of an individual IP measurement was 4–12%.

RESULTS AND DISCUSSION

The oscillatory behaviour was measured for BZ systems involving D-gluconic and D-galactonic acids, their lactones, and D-glucose or D-galactose as the substrates.

Typical oscillation patterns are shown in Fig. 1. The BZ systems with D-gluconic acid and its lactone exhibit identical induction periods, *viz.* 35, 16, and 5 min at sulfuric acid concentrations of 0.7, 1.5, and 3.5 mol l^{-1}, respectively. The oscillatory patterns are identical as well (Fig. 1, curves *2*, *3*), in line with the fact that the lactone transforms to the corresponding acid in acid solutions[14]. Identical oscillation patterns, however, were also observed for D-glucose (Fig. 1, curve *1*), only the induction period was longer. This suggests that during the (longer) induction period, D-glucose was transformed by the forming bromine to D-gluconic acid, and so it was D-gluconic acid rather

than D-glucose that acted as the active substrate in the oscillatory reaction. This hypothesis was corroborated by the following experiment. We added excess bromine to a D-glucose solution in 1 M H_2SO_4 (the rate constant of oxidation of this sugar by bromine in this medium is $k = 0.63 \cdot 10^{-4}$ s^{-1} at 25 °C (ref.[15]) and the half-life is 3 h). In 30 hours we removed the excess Br_2 by nitrogen purging, and added the calculated aliquot of the solution to the BZ system. The oscillatory patterns were identical with those shown in Fig. 1, curve *2*, as if the BZ system had been started up with D-gluconic acid.

Optical isomers, *viz*. the naturally occurring D-glucose and artificially synthesized L-glucose and the D- and L-arabinose pair, were also used as the BZ substrates. The oscillatory patterns for the D- and L-forms were identical in both cases. Hence, the functional properties of the isomers do not affect the mechanism of the BZ reaction (the chemical and physical properties of optical isomers are identical or very close to one another). We failed to measure the oscillations polarimetrically.

Comparison of the Induction Periods for the BZ Systems with D-Glucose and D-Galactose

The origin and length of the IP in oscillation reactions are closely related to the course of the reactions constituting Process *C* in the FKN mechanism. These primarily include reactions of bromine with the organic substrate and of the oxidized catalyst species with the latter. It is typical for the BZ systems with D-glucose and D-galactose, which do not react fast with Br_2, that Br_2 forms in them immediately on mixing the reactants and inhibits the BrO_3^- + Mn(II) reaction[16]. During the IP the system waits for the Br_2 concentration to decrease to a value allowing the system to oscillate. Bromine is removed from the system chemically, by the above-mentioned reactions of Process *C*, as well as physically, with the nitrogen stream. The IP is shorter in the system with D-galactose than in the system with D-glucose over a wide range of sulfuric acid con-

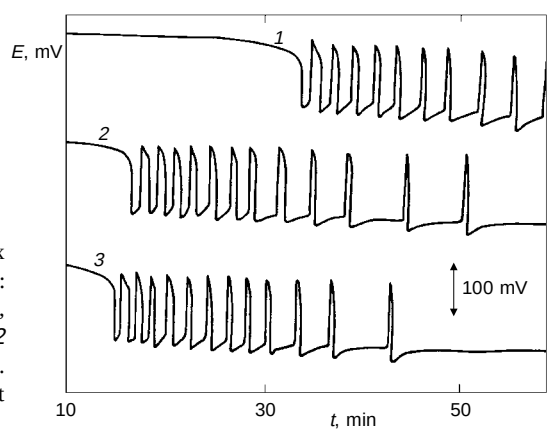

FIG. 1
Time dependences of Pt electrode redox potential. Starting concentrations (mol l^{-1}): H_2SO_4 1.5, $NaBrO_3$ 0.1, $MnSO_4$ 0.005, substrate 0.05. Substrate: *1* D-glucose, *2* D-gluconic acid, *3* D-gluconic lactone. Temperature 25 °C, nitrogen purging at 83.3 ml min^{-1}

centrations (Fig. 2). The former saccharide is more reactive than the latter (possesses a higher number of *cis*-glycol groups to bind to the reactant); for example, in 1 M H_2SO_4, D-galactose reacts with bromine and with Mn(III) 3-fold and 2.6-fold faster, respectively, than D-glucose[15]. The IP measured in the BZ systems in 1 M H_2SO_4 was 21 min for D-galactose and 55 min for D-glucose, in accordance with the rate of chemical removal of bromine from the system (physical removal was identical in both cases, determined by the nitrogen purging rate of 83 ml N_2/min).

Physical removal of bromine can be regarded as a 1st order chemical reaction, *viz*.

$$Br_2(solv) \xrightarrow{k_{Br}} Br_2(g) \ , \qquad (A)$$

where $Br_2(solv)$ is elementary bromine dissolved in the liquid phase, $Br_2(g)$ is bromine in the gas phase, and k_{Br} is the "rate constant" of the reaction.

The fact that Br_2, or Br^-, is responsible for the IP, was also proved by an experiment where to an BZ system with D-glucose in 0.06 M H_2SO_4 (IP = 0) was added NaBr in a concentration of 0.05 mmol l^{-1} (bromine emerged from the reaction $BrO_3^- + Br^-$), whereupon the IP increased to 54 min.

Dependence of the Induction Period on the Sulfuric or Perchloric Acid Concentration

The concentration of H_2SO_4 was varied over the range of 0.01 to 3.5 mol l^{-1} for D-glucose and D-galactose. The dependences of the IP on the sulfuric acid concentration exhibited a minimum and a maximum (Fig. 2, curves *1*, *2*). The analogous dependence for $HClO_4$ and D-glucose displayed a minimum.

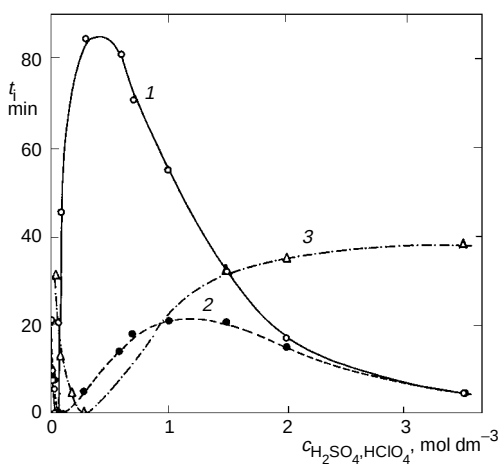

FIG. 2
Dependences of induction periods on sulfuric (*1*, *2*) and perchloric (*3*) acid concentrations. Starting reactant concentrations (mol l^{-1}): $NaBrO_3$ 0.1, $MnSO_4$ 0.005, substrate 0.05. Substrate: *1* D-glucose, *2* D-galactose, *3* D-glucose. Temperature 25 °C, nitrogen purging at 83.3 ml min^{-1}

The kinetics and mechanism of reaction of Mn(III) with D-glucose and D-galactose were investigated by the authors[15,17–19], who suggested an identical mechanism in which an Mn(III)–saccharide complex is first reversibly formed. This complex decomposes during the rate-determining step, where C–C bonds break down and highly reactive free radicals are formed. According to Doba and coworkers[18], the H^+ concentration affects mainly the rate of disproportionation of the complex, the rate constant increasing with the H^+ concentration increasing over the region of 0.03 to 0.34 mol l^{-1}. Ou and Jwo[15] observed a decrease in the rate of glucose oxidation by Mn(III) ions at higher sulfuric acid concentrations (above 1 mol l^{-1}) and suggested that this was due to the complex formation between manganese(III) and sulfates. Bakore and Barraria[17] assume that at high sulfuric acid concentrations, D-glucose is oxidized by the $[Mn(SO_4)_2H_2O]^-$ anion rather than by the Mn^{3+} cation. In perchloric acid solutions, Mn^{3+} ions and $MnOH^{2+}$ ions formed by the reaction $Mn^{3+} + H_2O \rightleftharpoons MnOH^{2+} + H^+$ are regarded[20] as the reacting species. The authors[15] reported an inverse proportionality between the rate constant of oxidation of glucose by Mn(III) ions and perchloric acid concentration. Over the region of higher perchloric acid concentrations (2–4 mol l^{-1}), however, the rate constant was virtually constant.

For the oxidation of glucose by bromine, the dependence of the rate constant logarithm on pH is linear over the region of pH 3–7, and attains a minimum and is very little pH-dependent at pH 0–3 (refs[21,22]). Presumably, neutral molecules of the saccharide are involved in the latter pH region, whereas oxidation of the anion predominates in the former pH region.

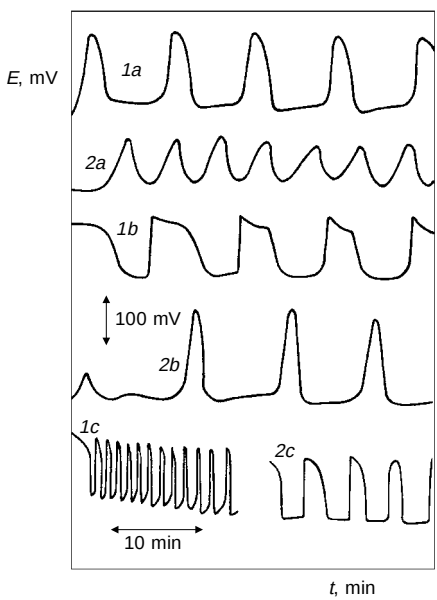

FIG. 3
Time dependences of Pt electrode redox potential for D-glucose as substrate in H_2SO_4 (*1*) and $HClO_4$ (*2*). Starting concentrations (mol l^{-1}): $NaBrO_3$ 0.1, $MnSO_4$ 0.005, D-glucose 0.05, H_2SO_4 0.06 (*a*), 0.1 (*b*), 2.0 (*c*). Temperature 25 °C, nitrogen purging at 83.3 ml min^{-1}. Oscillation patterns *1b*, *1c*, *2a*, *2c* recorded after the induction period

The Mn(III)–Br^- reaction should also be taken into account. It is supposed that species of the $MnBr^{2+}$, $MnBr_2^+$, $MnBr_3$, $MnOHBr^+$, and $MnOHBr_2$ type are formed[15]. The hydrogen ion dependence of this reaction is unknown.

Taking into account the above facts regarding the hydrogen ion dependence of the rate constants of the reactions responsible for the induction period and oscillation period in the BZ system, the dependence of the induction period on the concentration of H_2SO_4 or $HClO_4$ is not very surprising. The dependences as shown in Fig. 2, curves *1*, *3* demonstrate that the IP is longest in 0.3 M H_2SO_4 and is absent from the system with 0.3 M $HClO_4$. It is interesting that the two dependences intersect at an acid concentration of 1.5 mol l^{-1}; since oscillatory reactions of the BZ type have largely been examined at this concentration of the acid used, no differences have been observed in H_2SO_4 and $HClO_4$. The oscillatory patterns at identical concentrations of H_2SO_4 and $HClO_4$ are different (Fig. 3), suggesting that Mn(III) reacts in the form of different complex species exhibiting different reactivities.

The oscillation period decreased with the H_2SO_4 concentration in all of the systems examined.

Dependence of the Induction Period on Sulfuric Acid Concentration in the Closed System Without Nitrogen Purging

In 0.06 M H_2SO_4, the BZ system with D-glucose started to oscillate immediately on mixing the reactants (IP = 0). In such circumstances, the system also oscillated without nitrogen purging, in a closed (batch) system without stirring. Little amounts of Br_2 form at so low a concentration of H_2SO_4 and need not be removed physically. The system oscillates within the sulfuric acid concentration intervals (in mol l^{-1}) of ⟨0.03;0.2) for D-glucose and ⟨0.04;0.3) for D-galactose (Fig. 4). At H_2SO_4 concentrations lower than 0.04 mol l^{-1}, where the IP increases again, the cause of the IP may be the same as in the

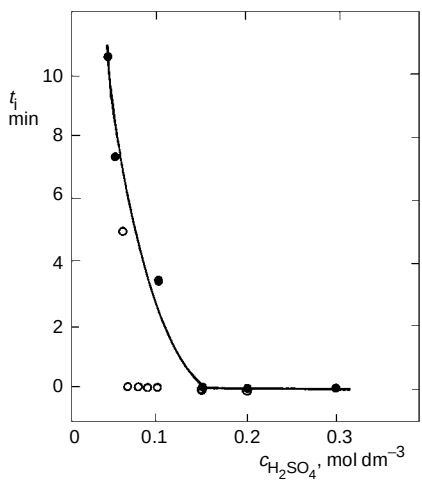

FIG. 4
Dependences of the induction period on sulfuric acid concentration in batch system without nitrogen purging. Starting concentrations as in Fig. 2, 25 °C. Open circles: D-glucose, full circles: D-galactose

classical BZ reaction, where a certain amount of Br^- or Br_2 must accumulate for the oscillations to start up.

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