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Simple $KBrO_3$, H_2SO_4 Batch Oscillator

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$KBrO_3$ and H_2SO_4 produce an oscillating system in batch when the proper combination of substrate concentrations, stirring rates, and temperatures is used. Bromide present as an impurity in $KBrO_3$ also takes part in the reaction. In many Belousov−Zhabotinsky (BZ) systems the above substrates are used and mixed with only an organic substance or with an organic substance and a catalyst, and the simple bromate oscillator cooperates with an organic substance, a catalyst, or both. The bromate oscillator found in this work is the simplest one in the BZ system composed of BrO_3^-, H_2SO_4, an organic substance, and a catalyst.

Introduction

Historically, the simplest oscillator of the Belousov−Zhabotinsky (BZ) type is composed of BrO_3^-, Br^-, H^+, and either Mn^{2+} or Ce^{3+} in a continuous flow stirred tank reactor (CSTR).[1,2] This system exhibits oscillations in the potential of a Pt electrode within very narrow regions of initial reagent concentrations and flow rate. Recently, Frerichs et al. observed evidence of nonlinear behavior in the $NaBrO_3-H_2SO_4$ batch system and also obtained oscillations in the Pt potential for the $BrO_3^- - Br^- - H^+$ system in batch.[3] Results from refs 1−3 were instrumental in undertaking the present work. In addition, a strong impetus for the present work was our results from a previous study.[4]

The chemical reaction of a BZ system, namely, malonic acid, ferroine, H_2SO_4, and $KBrO_3$, was investigated as a batch system in ref 4 utilizing Pt and Br^- ion-selective electrodes (ISE), while reaching an equilibrium state under the reported experimental conditions. In the equilibrium state there were no obvious oscillations observed at either of the electrodes. However, the time to reach equilibrium lasted longer in the case of the bromide electrode than in the case of Pt electrode. This is distinctly seen in Figures 1 and 2 where after the distance where oscillatory signals from the Pt electrode become steady, there are still three peaks recorded at the Br electrode in the first case and one peak in the second case. Similar results were reproduced in all experimental runs. Additionally, similar unusual behavior of the BZ reaction was also observed many times in a batch reactor following the CSTR experiments. In these experiments the CSTR reactor was changed into a batch reactor in which the electrodes were placed in a cover as is typical for a CSTR reactor. In the covered (there was no gap above the reaction mixture) experiments, gaseous products of the reaction could not easily escape from the chemical mixture. Accumulation of the gaseous products resulted in a diminishing of the electrode signals. Signals (in the meaning of oscillations) disappeared at the Pt electrode, while some signal oscillations were still seen at the Br^- ISE electrode. The gaseous product accumulated to sufficient pressure and quantity forcing some of the products to escape via the reactor cover. Following leakage of the gas products from the cover some oscillations appeared again at those electrodes, and usually oscillations seen by the Br^- ISE electrode lasted longer than oscillations seen by the Pt electrode as has been stated above. This situation was repeated in the system until equilibrium (at the estimated conditions) was reached. The experiment showed that a pure bromate oscillator (composed of $KBrO_3$ with small amounts of Br^-, as impurities, and H_2SO_4) can exist coupled with an organic acid and catalizer (in our previous experiments,[4] namely, with malonic acid, ferroin). However, although it will be shown that the bromate oscillator can exist alone as an independent oscillator, malonic acid and catalizer cannot exist alone as an independent oscillator. The malonic acid and catalizer can oscillate only when coupled with the bromate oscillator. The aim of this work was to demonstrate experimentally and in theory the existence of the bromate oscillator. Experimentally, the purpose of the work was to find concentrations of reagents, stirring rate, temperature, etc., i.e., some specific experimental conditions, which would demonstrate evidence of oscillations in such a simple system.

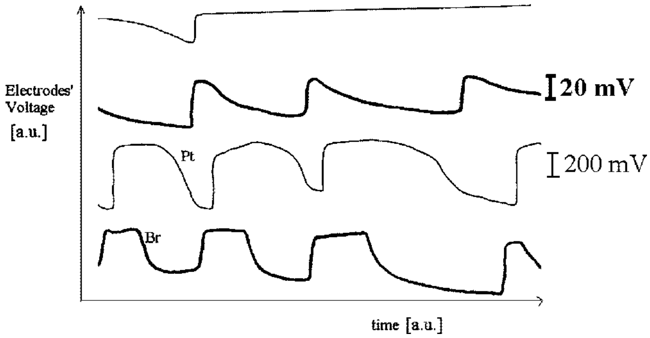

Figure 1. Batch experiment at 24.5 °C for the BZ system: $[\text{malonic acid}]_0$ 0.025 M, $[\text{ferroine}]_0$ 0.00338 M, $[KBrO_3]_0$ 0.19 M, $[H_2SO_4]_0$ 0.38 M at stirring rate equal to 740 rpm in a state close to the chemical equilibrium at those conditions. The experiment was in flowing nitrogen at a pressure of 1 atm above the surface of the reaction mixture. One can see signals from the bromide electrode (thick curve) and platinum electrode (thin curve) vs time. Those results were obtained only with the help of an MTA recorder (Kutesz, type 1040/4). On the picture we can distinguish two thick curves and two thin curves. In each case the second curve (of certain thickness) from the bottom is a continuation of the first curve from the bottom.

Reagents. Analytical grade chemicals, $KBrO_3$ ("POCh" S. A. Gliwice), H_2SO_4 ("POCh" S. A. Gliwice), were used without further purification. Noteworthy are the contents of the $KBrO_3$ package. The package labeling gives the following: $KBrO_3$ min 99.8%; S max 0.005%; Br max 0.02%; Cl, ClO_3 max 0.05%; SO_4 max 0.005%; heavy metals (Pb) max 0.0005%; Fe max 0.0005%; N max 0.002%; Na max 0.01%.

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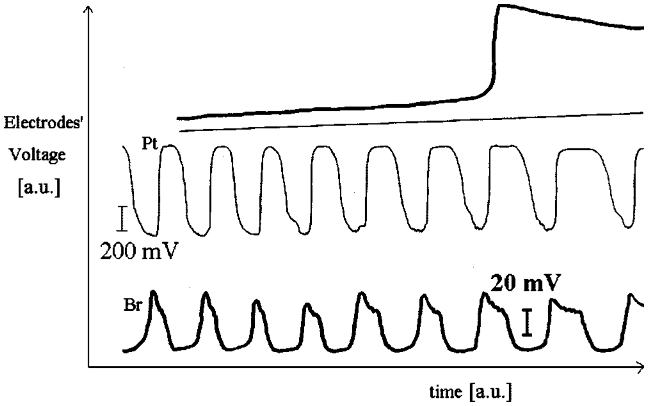

Figure 2. Same experiments as in Figure 1 but at a temperature of +21 °C.

Stock solutions of $KBrO_3$, H_2SO_4 were prepared using doubly distilled water.

Apparatus. A thermally insulated cylindrical glass vessel was used in all experiments (internal dimensions: diameter 37 mm, height 110 mm), and a rod-shaped Teflon-coated magnetic stirrer (length 21 mm, diameter 5 mm) was applied. The stirring rate was 600 rpm. In some cases the stirring rate was not equal to 600 rpm, but it was changed via a stepping process to greater, and later to smaller, stirring rates, in order to investigate the influence of the stirring rate on the oscillations. The volume of the entire reaction mixture was 40 mL. A saturated calomel reference electrode was used in the batch experiments to measure and record, via a 1 M KNO_3 salt bridge, the potential at the platinum electrode. Changing potentials versus time were recorded by an MTA (Kutesz, type 1040/4) recorder and by a PC computer.

Procedures. In our batch experiments the reaction was initiated by adding the H_2SO_4 solution into the $KBrO_3$ solution. In all experiments initial concentrations of the reagents were the same and equal to $[KBrO_3]_0 = 0.0125$ M, $[H_2SO_4]_0 = 0.32$ M. Finding the right initial concentrations of the reagents was not an easy task. As mentioned above in the Introduction, earlier results[4] prompted the initial concentration values. The oscillatory signal of both electrodes became steady very close to the equilibrium of the BZ reaction suggesting that the reagent concentrations (in the planned experiment) should be small relative to the initial concentrations. Particularly the bromate concentration had to be small relative to its initial concentration, whereas the concentration of H_2SO_4 was assumed to be equal to the value used in the experiments with malonic acid, discussed above. The temperature of the chemical mixture was thermostatically controlled at 25 °C during our experiments except for the fourth experiment where the temperatures of 20 and 28.9 °C were additionally used.

Results

Results of the six experimental runs are discussed here. After ca. 1 h from the start of the first experimental run, oscillations were observed on the Pt electrode with a period of oscillation equal to ca. 22 min and a potential amplitude ca. 10 mV. These oscillations were similar to those in both the second and fifth experimental runs described below. During the second experiment, oscillations began ca. 2 h after start of the run. The period of oscillations and the amplitude of oscillations were 18.5 min and 10 mV, respectively, on the first day of the first experiment. The mixture was kept at room temperature until the next day when oscillations were again observed at the Pt electrode, similar to those on the first day, but with a smaller period of oscillation, ca. 13.3 min. The same situation occurred again on the third day, but the period of oscillation increased to ca. 17.2 min. On the fourth day no oscillations were observed. In the third experiment (Figure 3) the first oscillations appeared about 6 h from the start of the run. Oscillations were observed on the Pt electrode with a period ca. 8.7 min but with smaller amplitudes than in the first two runs. Such small oscillations were observed also in the forth and sixth experimental runs. On the second day of the third experimental run oscillations continued. Oscillations occurred again on the third day until the moment when the stirring rate was reduced to ca. 300 rpm which terminated the oscillations.

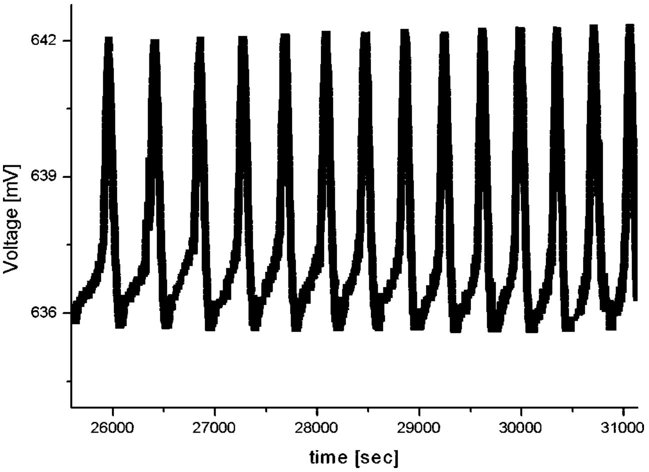

Figure 3. Experimental result from experiment number 3.

The fourth experiment also yielded oscillations ca. 5.5 h from the start of the experiment. During this fourth experiment the period of oscillations was measured at several temperatures. The period was 8.7 min at 20 °C, 7.8 min at 25.4 °C, and 7.5 min at 28.9 °C. These values were used to estimate the value of energy activation for the reaction. The fifth experiment yielded oscillations after ca. 20 min from the beginning of the reaction with a period of oscillation ca. 6.3 min. In the fifth experiment the influence of the stirring rate was investigated versus the period of oscillations. A stirring rate greater than 600 rpm yielded oscillations with a decreased period, ca. 6.3 min as noted above, while a lower stirring rate, namely, 300 rpm, increased the period to ca. 10.8 min. Stirring rates less than 300 rpm terminated the oscillations as in the second and third experiments. In the sixth experiment the first oscillations (with a period ca. 14 min) appeared 6 h from the very beginning of the experimental run. As in previous experimental runs, an increased stirring rate decreased the period of oscillations from ca. 14 to ca. 6.5 min.

At constant experimental conditions, i.e., the same temperature and stirring rate, the period of oscillations was observed to shorten with increasing time of some runs. At the end of the experimental runs, the period of oscillations increased to very large values, becoming infinite, because oscillations disappear at the end of the run.

One should add that some oscillations in the system BrO_3^-, H_2SO_4 were observed in the region of initial H_2SO_4 concentrations: 0.032 up to 0.875 M at the initial concentration of BrO_3^- 0.0125 M. In our experiment one could state also that the BrO_3^- initial concentration greater than 0.006 M and smaller than 0.019 M is important in order to observe oscillations (at 0.32 M initial concentration of H_2SO_4).

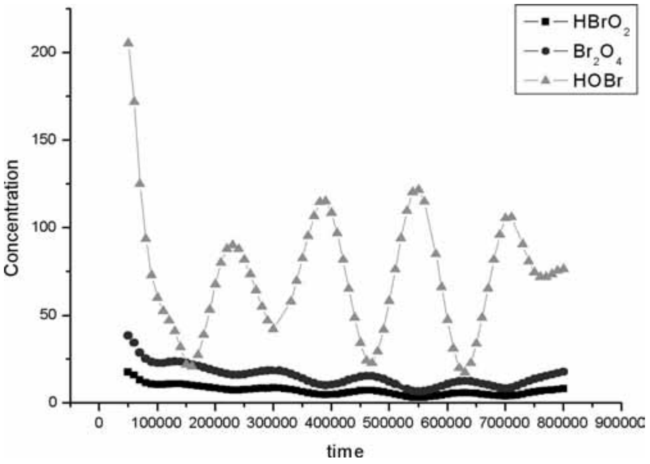

Figure 4. Dependence of $HBrO_2$, Br_2O_4, and HOBr concentration with time obtained using eqs 2−13.

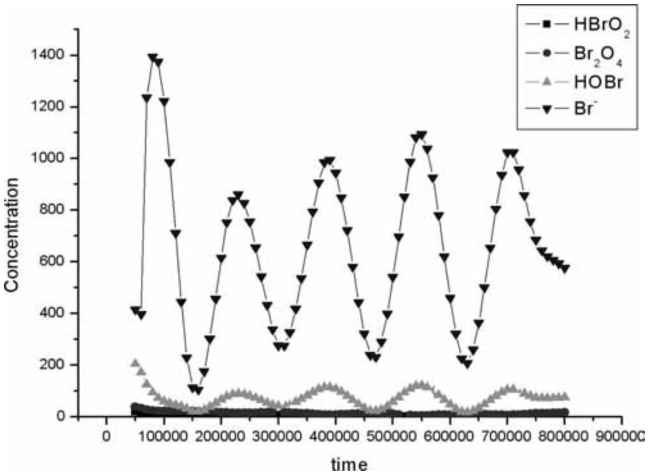

Figure 5. Dependence of $HBrO_2$, Br_2O_4, HOBr, and Br^- concentration with time obtained using eqs 2−13.

Discussion

From the results, one can state the following.

The simple system, composed of $KBrO_3$ and H_2SO_4, can oscillate within a region of reagent concentration, temperature, and stirring rate. Br^- takes part also in the reaction. Br^- was present in a small amount in the reaction mixture. Such a small amount of Br^- was connected with its presence as an impurity in $KBrO_3$.

The behavior of the system depends on both stirring rate and temperature. The first dependence, i.e., decreasing oscillations (and their disappearance) at reduced stirring rates, seems to be a very strong effect in comparison with the behavior of other BZ systems. The effect might even be called unusual.

In the reaction Br_2 is created rapidly. This can be concluded by observing the rate constant connected with the reaction producing Br_2 (in the reactions' set below). Smaller stirring rates yield lower rates of Br_2 removal from the solution. Hence, the rate of production of Br^- and HOBr increases, thereby affecting other chemical reagents coupled one to the other.

When the rates of production of Br^-, HOBr, $HBrO_2$, BrO_3^-, and Br_2O_4 are compared with their rates of decomposition we can make the following conclusion. Br^-, HOBr, $HBrO_2$, and Br_2O_4 disappear with time during the reaction (i.e., in the batch system). Although BrO_3^- is produced in reactions 3 and 8, its concentration cannot increase because in reaction 1 BrO_3^- produces HOBr and $HBrO_2$ disappearing in time with a great rate (reactions 4 and 6). The concentration of Br_2 increases with time. This result is responsible for the gradual disappearance of oscillations as was observed both experimentally and in simulations.

The production of HOBr is connected with the decomposition of $HBrO_2$ with a great rate (reactions 4 and 8). This fact is responsible for HOBr peaks on Figure 4 appearing at the minima of the $HBrO_2$ curve. It is true: eqs 2 and 3 show that production and decomposition of HOBr and $HBrO_2$ also take place on the way of eqs 2 and 3, but with much smaller rate as it was in the case of eqs 4 and 8.

Likewise, the great rate of HOBr decomposition (eq 6) by Br^- and H^+ is responsible for peaks on Figure 5 appearing at the same time for HOBr and Br^-.

The role of Br^- ions is as follows. Looking at eqs 2−13, we can see that in reactions 2, 4, and 6 they are exhausted, and in reactions 3, 5, and 7 they are produced, and that only reactions 4 and 6 are very fast ones. Therefore, they disappear in the reaction just the opposite to the typical BZ reaction where the end of the reaction at certain conditions is connected with an increase of Br^- concentration (as, for example, in ref 4). The role of Br^- is very important. Without Br^- the production of HOBr and $HBrO_2$ would be impossible. The last mentioned substances take part in many reactions (eqs 3−13) characterized by various values of their kinetic constants, and it has an influence on the oscillating behavior of some reagents' concentrations (against time), as we can see solving the differential equations (including all of them from $\dot{a}$ to $\dot{w}$).

Reproducibility of the behavior of the system was good but not so good as for other oscillating chemical systems.[4,9] Taking into account the amplitude of oscillations (ca. 10 or 5 mV) and the induction time which was varied from ca. 30 min to ca. 6 h, one can conclude that the system is very sensitive to a number of factors.

During the experimental runs, only decreasing periods of oscillations were observed until the oscillations totally disappeared. Disappearance of the oscillations can be interpreted as an increase of the period to infinity. In another BZ system, in a batch system, for example,[7] increasing periods of oscillations were observed in some experimental runs followed by decreasing periods when reaching an equilibrium (and at the very end of the reaction its great increase).

The behavior of the period of oscillations at the very beginning of the reaction at various temperatures, and using the well-known Arrhenius equation[15]

$$k = (\mathrm{const})(\exp(-\Delta E/RT)) \qquad (1)$$

where k means the rate constant of the process under consideration, provides the possibility to estimate the energy of activation for the reaction. The result obtained in this case is $\Delta E = 3.7 \pm 0.7$ kJ/mol. By [1/(period of oscillations)] we determine the rate constant. Such value was used as k to get ΔE from eq 1.

Taking into account known[5,10] Br compound reactions, the following equations, with associated rate constants, can be concluded:

$$Br^- + BrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2 \qquad 2\ M^{-3}\ s^{-1} \qquad [\text{ref } 10]\ (2)$$

$$HOBr + HBrO_2 \rightarrow Br^- + BrO_3^- + 2H^+ \qquad 3.3\ M^{-1}\ s^{-1} \qquad [\text{ref } 10]\ (3)$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr \qquad 2.0 \times 10^6\ M^{-2}\ s^{-1} \qquad [\text{ref } 10]\ (4)$$

$$2HOBr \rightarrow Br^- + HBrO_2 + H^+ \qquad 2.0 \times 10^{-5}\ M^{-1}\ s^{-1} \qquad [\text{refs } 5,\ 10]\ (5)$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad 2.3 \times 10^9\ M^{-2}\ s^{-1} \qquad [\text{ref } 5]\ (6)$$

$$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+ \qquad 2.0\ s^{-1} \qquad [\text{ref } 5]\ (7)$$

$$2HBrO_2 \rightarrow BrO_3{}^- + HOBr + H^+ \qquad 3.0 \times 10^3\ M^{-1}\ s^{-1} \qquad [\text{ref } 10]\ (8)$$

$$BrO_3{}^- + HOBr + \ + H^+ \rightarrow 2HBrO_2 \qquad 7.5 \times 10^{-9}\ M^{-2}\ s^{-1} \qquad [\text{ref } 10]\ (9)$$

$$BrO_3{}^- + HBrO_2 + \ + H^+ \rightarrow Br_2O_4 + H_2O \qquad 33.0\ M^{-2}\ s^{-1} \qquad [\text{ref } 10]\ (10)$$

$$Br_2O_4 + H_2O \rightarrow BrO_3{}^- + HBrO_2 + H^+ \qquad 2200\ s^{-1} \qquad [\text{ref } 10]\ (11)$$

$$Br_2O_4 \rightarrow 2BrO_2{}^{\bullet} \qquad 7.4 \times 10^4\ s^{-1} \qquad [\text{ref } 10] \quad (12)$$

$$2BrO_2{}^{\bullet} \rightarrow Br_2O_4 \qquad 1.4 \times 10^9\ M^{-1}\ s^{-1} \qquad [\text{ref } 10] \quad (13)$$

Reaction 2 above is made possible within the reactor due to the presence in the chemical mixture of BrO_3^- (coming from $KBrO_3$), H^+ (coming from H_2SO_4), and Br^- (present in $KBrO_3$ as the impurity). Reaction 2 produces HOBr and $HBrO_2$ which react, not only with each other, but with the substrates producing other compounds such as Br_2, Br_2O_4, and $BrO_2^{\bullet}$.

Some kinetic equations follow, using abbreviated symbols (see below) for the chemical reagents and products appearing in the above equations:

$$[Br^-] = a, \quad [BrO_3{}^-] = b, \quad [HOBr] = c, \quad [HBrO_2] = d, \quad [BrO_2{}^{\bullet}] = e, \quad [Br] = f, \quad [Br_2O_4] = g, \quad [H_2O] = w, \quad [H^+] = h$$

$$\dot{a} = -2abh^2 + 3.3cd - 2dah \times 10^6 + 2c^2 \times 10^{-5} - 2.3cah \times 10^9 + 2f^2w$$

$$\dot{b} = -33bdh + 2200gw - 2abh^2 + 3.3cd + 3000d^2 - 7.5bch \times 10^9$$

$$\dot{c} = 2abh^2 + 3.3cd + 4dah \times 10^6 + 4c^2 \times 10^{-5} - 2.3cah \times 10^9 + 2f^2w + 3000d^2 - 7.5bch \times 10^9$$

$$\dot{d} = -33bdh + 2200gw + 2abh^2 - 3.3cd - 2dah \times 10^6 + 2c^2 \times 10^{-5} - 2d^2 3000 + 15bch \times 10^9$$

$$\dot{e} = 14.8g \times 10^4 - 2.8e^2 \times 10^9$$

$$\dot{f} = 4.6cah \times 10^9 - 4f^2w$$

$$\dot{g} = 33bdh - 2200gw - 7.4g \times 10^4 + 1.4e^2 \times 10^9$$

$$\dot{h} = 33bdh + 2200gw - 2abh^2 + 6.6cd - 2dah \times 10^6 + 2c^2 \times 10^{-5} - 2.3cah \times 10^9 + 2f^2w - 7.5bch \times 10^9$$

$$\dot{w} = 33bdh - 2200gw + 2.3cah \times 10^9 - 2f^2w$$

These equations are in accordance with the "mass action law." Rate constants correspond to those obtained experimentally. Numerical simulations were performed using Mathematica software.

Initial reagent concentrations were taken from the experiments. However, in the case of the initial concentration of Br^-, i.e., $[a]_0$, the amount of Br^- in $KBrO_3$ was known to be maximum 0.02%. Figures 4 and 5 show oscillating behavior with $[a]_0 = 0.000\,000\,05$ M (estimated to be less than 0.02%) and with initial concentrations $[b]_0 = 0.0125$ M, $[h] = 0.64$ M, $[w]_0 = 55$ M (from the experimental values). One should add that the experimental 0.02% Br^- in $KBrO_3$ corresponds to an initial concentration of Br^- equal to 0.000 005 M. This last value is 100 times greater than the value used in the simulation (0.000 000 05 M), but it was necessary to use this smaller concentration of Br^- (at fixed other values and taken exactly from the experiment) in order to get an oscillating behavior of some reagents in the simulation. It should be noted that the amount of Br^- in $KBrO_3$ shown on the packing label of the $KBrO_3$ is a maximum of 0.02% (in reality the amount of Br^- in $KBrO_3$ is equal to 0.015%). The value used as $[a]_0$ in the simulations is less than 0.02%, i.e., 0.0002%, as mentioned above. The simulations are, however, successful when using the experimental values for the initial concentrations. This situation is often not the case (for example, ref 6), nor is it difficult to understand, if we take into account possible errors of the kinetic constants, "sensitivity" of differential equations to initial concentrations of reagents and of course formulation of the kinetic equations (where kinetic constants play an important role).

Concerning Figures 4 and 5, it appears the period is about 48 h (in simulation), not minutes (as in the experiment), suggesting that the model will undoubtedly need refinement. We note some oscillations appear after 100 000 s in the simulation while in the experiment oscillations appear after ca. 25 000 s (Figure 3) from the very beginning. We suggest that further work be undertaken where investigations of the BrO_3^-, Br^-, H_2SO_4 oscillator are conducted using an amount of Br^- clearly defined, and not simply estimated as impurities, as was the case in this work.

In Figures 4 and 5, concentrations of some important reagent substances, HOBr, Br^-, $HBrO_2$, and Br_2O_4, are seen to oscillate. In Figures 4 and 5, the time dependence of [HOBr] and $[Br^-]$ are observed with the maxima occurring simultaneously. The same situation is observed for $HBrO_2$ and Br_2O_4; however, the maxima for HOBr and Br^- correspond to minima for $HBrO_2$ and Br_2O_4.

In ref 10 system behavior is described by several chemical reactions which are compatible with reactions 2, 4, 6, 8, and 10 presented in this work. Additionally, there appear two reactions connected with oxidation of Ce^{3+} and with reduction of Ce^{4+}:

$$Ce^{3+} + BrO_2{}^{\bullet} + H^+ \rightleftarrows Ce^{4+} + HBrO_2 \qquad (a)$$

where the kinetic constant for the right-linked reaction is equal to $6.5 \times 10^5\ M^{-2}\ s^{-1}$, and for the left-linked reaction, in the opposite direction, is equal to $2.4 \times 10^7\ M^{-1}\ s^{-1}$, and

$$Ce^{4+} + BrO_2{}^{\bullet} + H_2O \rightleftarrows Ce^{3+} + BrO_3{}^- + 2H^+ \qquad (b)$$

where the kinetic constant for the right-linked reaction is equal to $9.6\ M^{-1}\ s^{-1}$, and for the left-linked reaction, in the opposite direction, is equal to $1.3 \times 10^{-4}\ M^{-3}\ s^{-1}$.

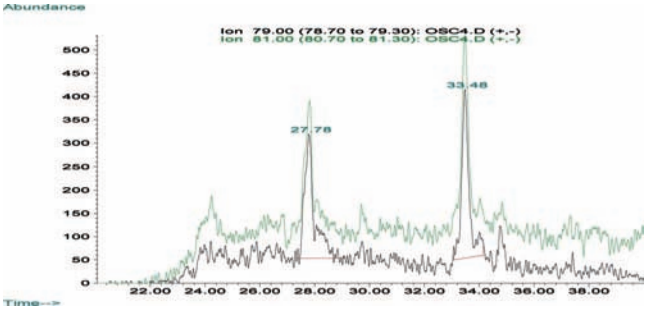

Figure 6. Chromatogram recorded for headspace gas over the chemical mixture.

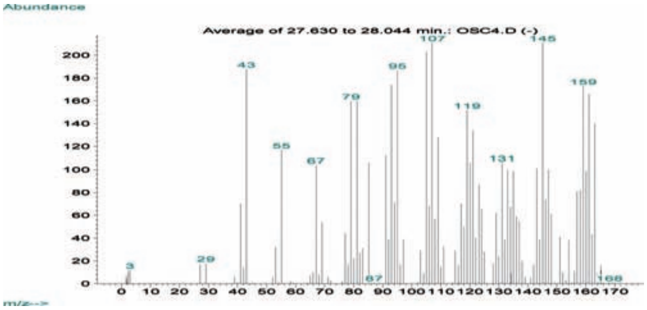

Figure 7. Mass spectrum of the peak at the retention time of 27.78 min.

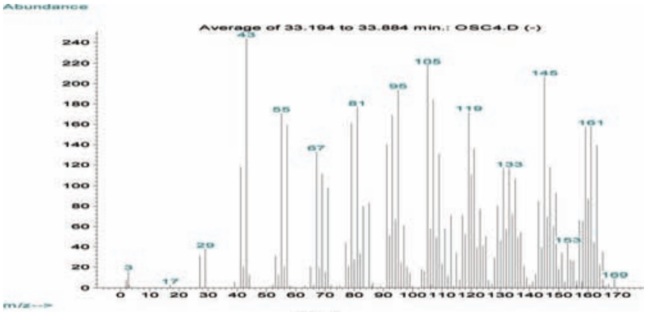

Fig. 8

Figure 8. Mass spectrum of the peak at the retention time of 33.48 min.

We can see that here the oxidation of Ce^{3+} and reduction of Ce^{4+} occurs in the presence of $BrO_2^{\bullet}$ radicals, whereas in some "normal" BZ reactions, having an additional organic substance present, the reduction process of Ce^{4+} takes place due to the presence of the organic substance.

In ref 14 we find the two following equations demonstrating the role of a catalyst in the simplest oscillator to date:

$$\mathrm{Br(V)} + 4\mathrm{Red} \rightarrow \mathrm{Br(I)} + 4\mathrm{Ox} \tag{A}$$

and

$$\mathrm{Br(I)} + n\mathrm{Ox} \rightarrow \mathrm{Br}^- + \mathrm{X} \tag{B}$$

where Red indicates the reduced form of catalyst metal ion, Ox indicates the oxidation state of the catalyst, X indicates a complex mixture of compounds (for example, the reduced form of catalyst). It is observed that reaction A corresponds to reaction 2 above and reaction B corresponds to reaction 3, where Red indicates Br^- and Ox indicates $HBrO_2$, nOx indicates HOBr, and X indicates BrO_3^-. Further, it can be seen that the other compounds connected with the organic substance can play the role of Ox or Red in a system containing an organic substance in addition to the bromate, catalyst, and sulfuric acid.

The kinetic constants of reactions 4, 6, and 8 were changed in ref 2 to get a better simulation of the specific regions of a phase diagram, which was not the case in this work. The system investigated in this work reminds one of another oscillator—ClO_2^-, I^-, H^+—which was investigated in the mixture with malonic acid.[13] In the case of our work, instead of ClO_2^- we used BrO_3^-, instead of I^- we use Br^-.

Analysis of the Gaseous Products over the Surface of the Chemical Mixture

An analysis of the gaseous products over the surface of the chemical mixture has been done by use of an HP 6890 series GC system chromatograph (Hewlett-Packard) coupled with a P 5973 mass-selective detector. Five times the analysis was carried out for the scan mode range of m/z 1.6−170. The results are shown on Figures 6−8.

Taking into account the appearance of the peaks shown on Figures 6 and 7, one can estimate some components of the gaseous mixture. The result is the following: Br, BrO, Br_2, and BrO_2 are present in the gaseous products in an amount getting smaller in the direction from Br to BrO_2. In spite of it one can find also an evidence of small amount of BrO_3, HBr, and a rather great amount of BrO_4. The last product appears in the chromatogram because we applied the temperature changing from 40 to 250 °C (in order to make faster the process of absorption and the inverted one, needed for analysis in the mass-selective detector). In such conditions we needed ca. 40 min for appearance of two peaks on the chromatogram. In shorter retention time we have not observed any peaks on the chromatogram.

The gaseous products of the reaction can take part in the reaction on the way determined by their solubility in the experimental conditions.

Behind the oscillations the system produces Br_2 which is responsible for the yellow color appearing in the chemical mixture. The color gets more intense if the mixture of $KBrO_3$ and H_2SO_4 is maintained longer.

Conclusions

It can be concluded that mixing BrO_3^- and H_2SO_4 produces an oscillating system in batch when using the proper concentrations of substrates, stirring rates, and temperature. Bromide present as an impurity in $KBrO_3$ also takes part in the reaction. In many BZ systems those substrates (BrO_3^- and H_2SO_4) are used and mixed with only an organic substance[6] or with an organic substance and with a catalyst.[7,8] Hence, the bromate oscillator cooperates with an organic substance and a catalyst, or with only a catalyst, or with an organic substance. The bromate oscillator is the simplest one in the BZ system composed of BrO_3^-, H_2SO_4, an organic substance, and a catalyst. The oscillating system without an organic substance (i.e., composed of BrO_3^-, H_2SO_4, Br^-, and catalyst) stated at the beginning of the work was observed many years ago.[1,2,11] It can also be concluded that the richness of Br compound chemistry is responsible for such behavior. It should also be mentioned that MnO_4^-, $Cr_2O_7^{2-}$,ClO_3^-, or JO_3^-, which oxidize most organic compounds, do not bring about chemical oscillation.[12]

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