Oscillations of the Bray−Liebhafsky Reaction at Low Flow Rates in a Continuous Flow Stirred Tank Reactor

Frank G. Buchholtz* and Sebastian Broecker

Institute of Physical Chemistry, Univeirsity of Würzburg, 97074 Würzburg, Germany

Received: October 16, 1997; In Final Form: December 31, 1997

The iodate-catalyzed decomposition of hydrogen peroxide in an aqueous solution of sulfuric acid is carried out in a continuous flow stirred tank reactor for various reactant concentrations and flow rates. Period-one oscillations of the iodide concentration are found. They show similar shape and dependences on inflow concentrations as the corresponding batch system. Only residence times of more than 39 min can sustain oscillations. We conclude that the lack of an overlying gas phase prevents oscillations at shorter residence times, which have been observed earlier with a different experimental setup.

Introduction

The oscillations in the iodate-catalyzed decomposition of hydrogen peroxide in acidic medium, known as the Bray−Liebhafsky (BL) reaction, were discovered eight decades ago.[1] Since then, the investigations of this reaction have been performed mostly in the batch system.[2] The only examination of the reaction in a continuous flow stirred tank reactor (CSTR) was carried out in 1978 by Chopin-Dumas and Pacault,[3] who used an overflow CSTR with an overlying gas phase and monitored the iodide concentration potentiometrically.

The existence of a gaseous phase above the reaction medium was for a long time considered necessary for the occurrence of oscillations.[4] In addition to the reaction kinetics, physical phenomena, such as the exchange of oxygen and iodine between the liquid and the gas phase, were regarded to be essential for the oscillations. Recently, an investigation of the effect of high pressures on the BL reaction by Laurenczy and Beck[5] questioned this assumption. They concluded that the escape of oxygen from the liquid phase is not vital for the oscillations.

We address in this paper the problem of oscillations in a single-phase CSTR and their relation to previous observations in batch. We also analyze the influence of the reactant concentrations and the flow rate on the oscillatory behavior of the BL reaction.

Experimental Section

The experiments were carried out in a well-stirred 7.8 mL thermostated continuous flow stirred tank reactor (CSTR) at 333.0 ± 0.2 K (60 °C) fitted to two syringes in a high-precision pump which is controlled by a computer. The thickness of the electrode required such a relatively large volume of the reactor. The cylindrical CSTR has two inlet tubes at the bottom and one outlet tube at the top. Mixing by a magnetic stirrer occurred at the bottom. The time-dependent change of the iodide concentration was monitored by an iodide-selective electrode (WTB J500) against a platinum electrode. A concentration change by a factor of 10 was calibrated to a voltage change of 200 mV. Unless stated otherwise, the residence time was kept at 9600 s because this was found to be a good experimental value for oscillations at a wide range of concentrations. Usually, a transient time of 2 h was allowed to elapse before oscillations were monitored. A spectroscopical measurement of the iodine concentration, as it is normally used for batch experiments, was found to be too invasive to the system in that it can by itself generate oscillations. We did not monitor the concentration of oxygen because of the formation of gas bubbles in the CSTR.

For a fixed hydrogen peroxide concentration of 0.2 and 0.125 M [H^+] at a residence time of 9600 s, we varied the iodate concentration from 0.03 up to 0.15 M. At an iodate concentration of 0.03 and 0.125 M [H^+] we tested hydrogen peroxide concentrations in the range 0.007−0.2 M for the same residence time. We varied the residence time in the range of 2000−15 000 s while keeping inflow concentrations at 0.03 M for KIO_3, 0.2 M for H_2O_2, and 0.125 M for H^+. The stirring rate of the magnetic stirrer was kept constant at a rate of about 700 rpm. Illumination with ordinary neon lamps was held unchanged. The used chemicals were potassium iodate p.a. (Riedel-de-Haen), hydrogen peroxide 30% p.a. (Merck), and sulfuric acid (Riedel-de-Haen). The two syringes in the precision pump were filled with two solutions: one containing potassium iodate and the other acidic hydrogen peroxide at various concentrations. The values for the concentrations refer to those inside the reactor.

Results and Discussion

Our experiments show that at long residence times (about 2.5 h) the oscillating behavior of the iodide concentration in the BL reaction in a CSTR depends on the concentrations of the reactants as well as on the flow rate. No investigation of the influence of the hydrogen peroxide concentration in a CSTR has been performed before. As can be seen in Figure 1, the hydrogen peroxide concentration has a big influence on the frequency of the oscillations in a CSTR but little influence on the amplitude of the oscillation. The period lengthens when the concentration of hydrogen peroxide is reduced (Figure 2).

Anić and Kolar-Anić[6] found similar results in batch experiments. They could only show this dependence using the mean length of period because in batch systems the period of oscillations is affected by the gradual decline of hydrogen peroxide. In a CSTR the concentration of hydrogen peroxide could be varied within a wide range (0.0075−0.2 M) without

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* Corresponding author. e-mail buchholt@phys-chemie.uni-wuerzburg.de; FAX 0049-931-888-6302.

S1089-5639(97)03362-8 CCC: $15.00 © 1998 American Chemical Society
Published on Web 02/10/1998

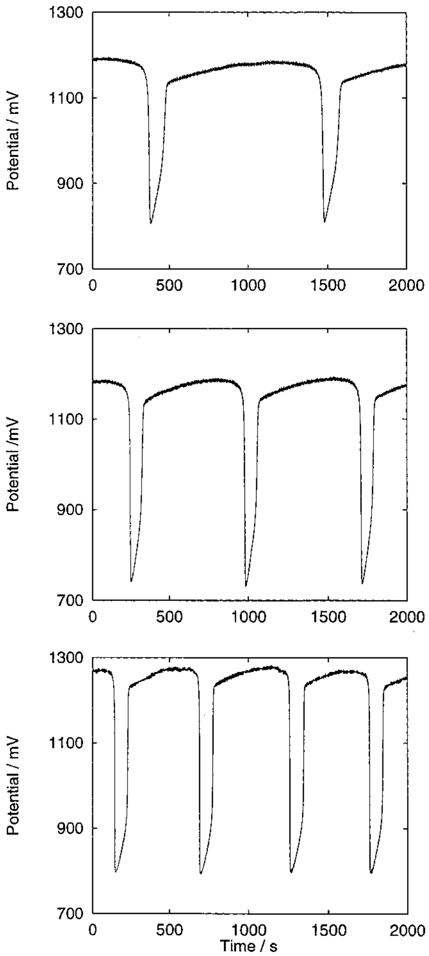

Figure 1. Potentiometric recording of the iodide concentration at different inflow concentrations of H_2O_2: upper trace, 0.02 M; middle trace, 0.05 M; lower trace, 0.2 M. Initial time is chosen arbitrarily.

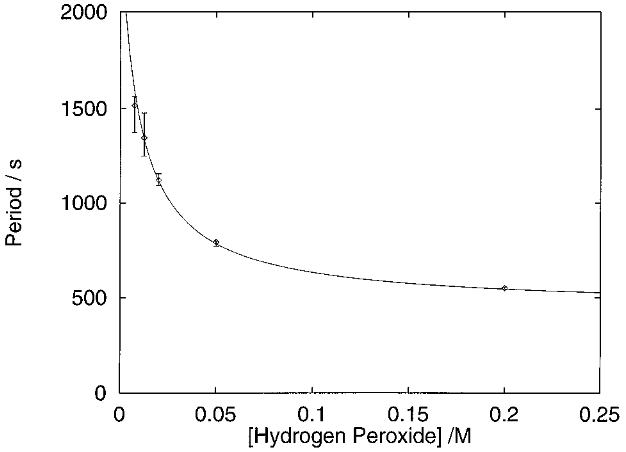

Figure 2. Dependence of the period on the concentration of hydrogen peroxide. Error bars indicate that longer periods show larger variations whereas shorter periods are very regular.

leaving the oscillatory region. The lower concentration limit is difficult to determine experimentally because the period of oscillation tends to be less stable and can exceed 1000 s with these parameters. The oscillations are damped at very low hydrogen peroxide concentrations. In the latter case we studied the long-term behavior (about 20 000 s) of the iodide concentration. At all concentrations of hydrogen peroxide, only period-one (P1) oscillations have been found. As can be seen in Figure 3, the relatively high temperature of 60 °C and the evolution of

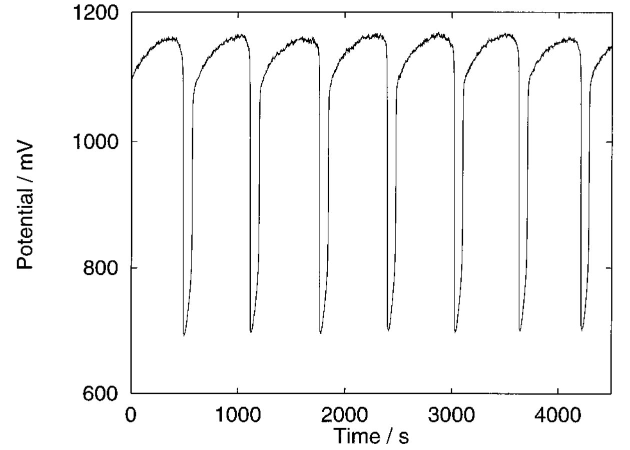

Figure 3. Potentiometric recording of the iodide concentration with inflow concentrations of H_2O_2 (0.2 M), KIO_3 (0.03 M), and H^+ (0.125 M). Residence time: 9600 s.

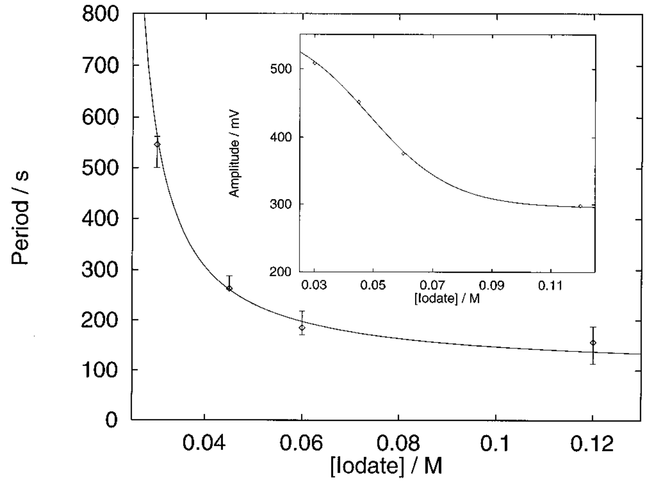

Figure 4. Dependence of the period and the amplitude (inset) on the concentration of iodate.

oxygen does not impair the appearance of regular oscillations over a rather long time interval.

The variation of the iodate concentration shows stronger effects than changes of the hydrogen peroxide concentration in that it influences both the frequency and the amplitude of the oscillations. An increase of the iodate concentration brings about a decrease in both the period and the amplitude of the oscillations as is shown in Figure 4. A similar result was observed in the two-phase CSTR by Chopin-Dumas and Pacault,[3] although some of their measurements were done at higher temperatures. Anić and Kolar-Anić[7] found a similar dependence in their batch system. Our experiments show that oscillations exist in a large concentration range for iodate (0.03–0.12 M). This is approximately the range described for the two-phase CSTR.[3] Again only P1 oscillations are found. The P2 oscillations of iodine, which were observed in a batch system by Vavilin et al.,[8] could not be reproduced as a stable pattern in our CSTR. It was only with oxygen-saturated reactant solutions and during a transient interval of 10 min that P2 behavior could be seen in the iodide concentration.

A variation of the concentration of iodate affects the shape of the iodide oscillations. During the reduced phase at high potentials, between two minima, the iodide concentration declines when the iodate concentration is high. The opposite effect, namely a rise of the iodide concentration during this phase, occurs when instead of the iodate concentration the

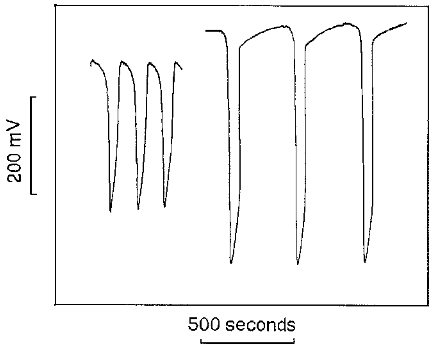

Figure 5. Potentiometric recording of the iodide concentration at different inflow concentrations. Changes with respect to Figure 3 are (left trace) 0.12 M iodate and (right trace) 0.05 M hydrogen peroxide. Note that amplitude and frequency are affected.

hydrogen peroxide concentration is increased (see Figure 5). Chopin-Dumas and Pacault observed a similar effect when they varied the temperature instead of the concentration of a reactant.[3]

If the acidity of the system is changed, the experiments become quite difficult to reproduce because the system is extremely sensitive to changes of the H^+ concentration, as Odutola et al.[9] have shown for the reaction in batch. The region of oscillations depends on the acidity which for the above given experimental parameters in the CSTR ranges approximately from 0.09 to 0.13 M. This range is narrower than the one found in the two-phase CSTR at high flow rates. For experiments in batch, even a much lower acidity of the system is sufficient to sustain oscillations. With decreasing acidity the period of oscillations is significantly prolonged; e.g., at a H^+ concentration of 0.107 M and at the given reaction parameters, the period of oscillation can exceed 2500 s. At acidities lower than 0.1 M, the high potential phase of the oscillations becomes "noisy" and the rate of formation of iodide is decreased.

Some of our results are in agreement with those found in the partly comparable measurements by Chopin-Dumas and Pacault.[3] However, the differences in experimental conditions do not allow a complete comparison. While their group observed oscillations of the iodide concentration at a high flow rate (with a residence time of about 10 min), we found oscillations at quite long residence times (in a time scale of hours). Our experiments do not show any oscillations at higher flow rates. We attribute the discrepancy between our results and theirs to the differences in the experimental setup. In our case, there was no gas phase above the solution in the reactor, whereas the other group used a two-phase overflow CSTR. There are also differences in the volume and shape of the reactors, in the mixing rates, and, most important, in the used H^+ concentration, which is a very influential parameter. It is possible that the differences between the two experimental systems are responsible for the observation of oscillations at totally different flow rates. We found the typical form of oscillations in good agreement with the known CSTR experiments.

A variation of the flow rate in the range of 10^{-4} to 5.5×10^{-4} s^{-1} for the inflow concentrations of iodate (0.03 M), hydrogen peroxide (0.2 M), and H^+ (0.125 M) shows that the amplitude of the oscillations decreases until a steady state is reached when the flow rate is increased (see Figure 6). The period of oscillations is affected to a smaller extent than the amplitude. At a flow rate of 4.3×10^{-4} s^{-1} damped oscillations lead to a steady state. This behavior indicates the presence of a supercritical Hopf bifurcation at the critical point. The diagram in Figure 6 illustrates the dependence of the amplitude and frequency on the flow rate.

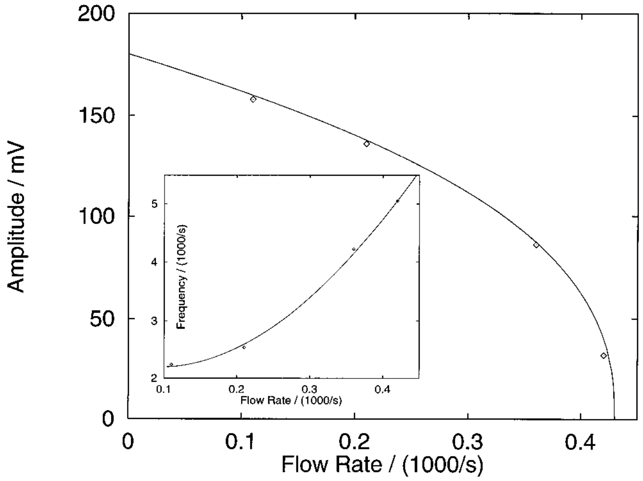

Figure 6. Dependence of the amplitude and frequency (inset) on the flow rate.

The most intriguing feature of the examinations is the fact that the BL reaction shows at a wide range of reactant concentrations only P1 oscillations at low flow rates in a CSTR at nearly all examined concentrations. This is in good correlation with the known experiments for the batch system[6,7] and in the two-phase CSTR at high flow rates.[3] It is only at higher acidity level that the system may switch unpredictably between regular large P1 oscillations and small oscillations of high frequency at a low mean iodide concentration. This behavior resembles the typical mixed-mode oscillations in the Belousov–Zhabotinsky reaction in which a switching between a primary Hopf bifurcation and a secondary bifurcation has been found.[10] A similar phenomenon has been reported, but not explained, by Chopin-Dumas and Pacault[3] with the two-phase CSTR at high flow rates and high acidity. In our experiments, the time that the reaction spends in oscillations of small amplitudes can be prolonged by a small temperature decrease (about 1–3 °C). A relationship between the two most influential parameters, namely the temperature and the acidity, is in agreement with the observations in the batch system by Anić et al.[11] According to their conclusion, an increase of the acidity produces a similar effect as a decrease of temperature. The influence of the temperature on the BL reaction in the CSTR at low flow rates will be examined in a further publication.

Conclusion

It should be noted for purposes of constructing a mechanism that the experiments reported here are the first ones to be performed without a gaseous phase above the liquid phase. The gaseous phase was assumed[4] to be necessary for the appearance of the oscillations, which were believed to be the result of a combination of the chemical reaction and the physical exchange of gaseous products. Some hints that the presence of a gas phase above the reaction mixture is unnecessary for the occurrence of oscillations have been given by Laurenczy and Beck,[5] who showed that oscillations in this reaction are possible even at high pressure (up to 2000 bar).

In batch systems the rate of escape of gaseous products was found to influence the oscillations. By contrast, the CSTR provides the possibility of removing intermediates and products through the outflow which can be controlled and measured. Furthermore, the outflow affects all reactants in the same way, unless bubbles are formed. Therefore, the CSTR constitutes a better means of collecting reliable data that can be used for constructing a mechanism for the reaction.

One can conclude from the results that the principal reason for the oscillations in the BL reaction is chemical and that the interaction with an overlying gas phase contributes to changes in the location of bifurcation points but not to the existence of oscillations. We believe that this argument also holds for the batch system. This is in agreement with the high-pressure experiments of Laurenczy and Beck in the batch system.

Furthermore, the oscillations of the BL reaction in the CSTR are only possible at low flow rates under the experimental conditions applied here. This observation suggests that a close correlation exists between oscillations in batch and in a CSTR at flow rates where washout of intermediates and products is sufficiently slow.

Acknowledgment. We thank F. W. Schneider for helpful advice and the Deutsche Forschungsgemeinschaft for financial support.

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