J. Phys. Chem. A **2009,** *113,* 3127–3132

A Simple Method of Gas Evolution Measurement Suitable for Analysis of Batch Oscillating Reactions: Briggs−Rauscher System with Acetone Revisited

Erik Szabo and Peter Ševčík*

Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovak Republic

Received: November 12, 2008; Revised Manuscript Received: January 9, 2009

A high-precision batch-mode technique of gasometric measurement, employing weighing of liquid displaced by the gas, is proposed and supported by a detailed protocol for correct evaluation of the experimental data acquired. Results of measuring the gas production in the Briggs−Rauscher reaction with acetone, recorded following the procedures suggested, and precautions to be taken to enhance their reproducibility are discussed, and a previously undetected structure of the gas evolution rate peaks is reported.

1. Introduction

Oscillating chemical reactions exhibit emergent behavior of complexity not present in systems of independent processes. They relate significantly to a broad spectrum of other subjects of nonlinear dynamics,[1] and they make an important contribution to our overall comprehension of the nonlinear phenomena.

By far the most studied chemical oscillators are based on the complex chemistry of the halogens.[2−4] The classical Belousov−Zhabotinsky (BZ) reaction[5,6] corresponds to bromination and oxidation of malonic acid (MA) by acidic solutions of bromates in the presence of Ce ions, and the detailed kinetic investigations by Field, Körös, and Noyes[7] revealing the chemistry behind the oscillations of this system represent a cornerstone work in the research of chemical oscillators. The system composed of acidic solutions of H_2O_2 and iodate ions is known as the Bray−Liebhafsky (BL) oscillator,[8,9] and combined with MA and Mn ions as the catalyst, it gives rise to another distinct oscillating chemical system, known as the classical Briggs−Rauscher (BR) reaction.[10]

All the three reactions mentioned are conventionally considered to represent homogeneous oscillators, and the mechanisms of the oscillations emerging in the concentrations of the catalysts and the intermediates are traditionally assumed to be of purely chemical origins.[2−4] However, some extent of gas production actually accompanies all of these oscillations;[5,6,8−10] despite the fact that the chemical processes, with no doubt, play an absolutely essential role in their mechanisms, another type of oscillating chemical system, known as the gas evolution oscillators (GEOs), has demonstrated that, due to the highly nonlinear character of the process of bubble nucleation,[11] the evolution of gas from solutions often represents a cause of oscillations in its own right.[12,13]

Even though the prominently physical mechanism of such oscillations obviously remains essentially different from the mechanisms of the homogeneous oscillations driven mainly by the underlying chemistry, a significant body of research suggests the two classes of oscillators may not be completely unrelated. Various effects of the stirring rate, without doubt essential for the physical oscillations of the GEOs, have also been reported for all three: the BZ, the BL and the BR oscillating reactions.[2,3,14−28] Although in the continuously stirred tank reactors (CSTR) these effects can occur mainly due to imperfect mixing of the feed streams,[2,14] the mechanisms suggested for explaining the stirring effects in batch reactors are much more subtle. They include not only the effect of oxygen on the chemistry of the reactions,[15−17] concentration fluctuations,[18−21] or the stirring-dependent rate constants of diffusion-controlled reactions[22] but also the influences of stirring on the transport of volatile regulatory intermediates to the gas phase,[23−25] which has also been repeatedly discussed in connection with refining the mechanisms of these reactions.[26−28]

Furthermore, the possibility of a supersaturation buildup, which also is an essential feature of the GEOs, has been recently reported for the modified BZ oscillation reaction with acetonedicarboxylic acid, conducted without stirring.[29] Altogether, these results indicate that there is, most likely, a whole range of currently unknown complex physicochemical phenomena that may occur in the homogeneous oscillating reactions due to the specific interplay between the chemical and the physical aspects of the processes. Exact analysis of the evolution of gas in chemical oscillators is a necessary step in the research of these effects and a reliable method of its measurement is therefore required.

Production of gas in both the BZ and the BR reactions has been recently monitored by employing a flow-mode method of detection:[30−32] N_2 carrier gas removing the gases from the reaction matrix was mixed with H_2, the oxides of carbon were converted to CH_4 on a Ni catalyst, and finally, the concentration of CH_4 in the carrier gas was measured by the means of a flame ionization detector (FID), detecting well-defined oscillations in the rate of production of both CO_2 and CO. Other results, however, indicate that purging the reaction mixtures of its volatile components with N_2 may influence the overall course of the oscillations significantly,[33,34] and a batch-mode measurement might, therefore, afford results substantially different.

Nevertheless, as the batch-mode setups for high-precision experimental work with gases usually involve a great deal of practical difficulty, no method that would be suitable for such comparable batch-mode measurements of gas evolution in chemical oscillators, usually also simultaneously monitored potentiometrically, has been previously established. Several high-precision and fully automated techniques of gasometry (in the classical sense of word) have been proposed, either making use of the highly sensitive pressure sensors in isochoric

---

* Corresponding author. E-mail: sevcik@fns.uniba.sk.

10.1021/jp809969e CCC: $40.75

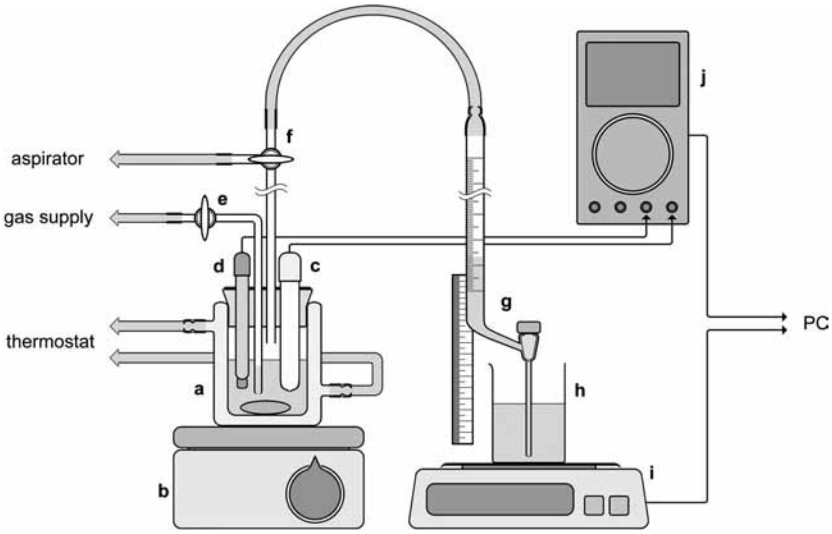

Figure 1. Apparatus employed to record evolution of gas in oscillating reactions by weighing of liquids displaced, while simultaneously monitoring changes in the composition of the reaction mixtures potentiometrically. For detailed specification of components a−i, as well as the description of the operation of the apparatus, refer to section 2.

measurements[35] or employing laser or electric monitoring of liquids confined to very small volumes of capillaries.[36,37] Nevertheless, the manual method, using a reservoir with water that is displaced by the gas into a burette, implemented in the batch-mode measurements of gas production in the BL[27] and the modified BR reaction with acetone,[28] which is one of the most spectacular homogeneous chemical oscillators at the same time evolving gas, remained the only method allowing simultaneous potentiometric monitoring of the reaction by macroelectrodes and was also employed for the recent measurements of supersaturation in the modified BZ reaction.[29]

Not even mentioning the great tedium involved, precision of this technique was, however, considerably limited because of the quantization of volumes recorded into whole drops leaving the reservoir and, of course, because of taking the readings of these volumes visually. The present paper, therefore, proposes and assesses a novel high-precision method of (approximately) isobaric batch-mode gasometric measurement, based on weighing the liquid displaced from a reservoir, and the most necessary corrections, to be taken into account in the protocol of measurement evaluation, are also discussed. Furthermore, the paper also presents and discusses the results of employing this technique for systematic reproduction of the measurements of gas production in the BR reaction with acetone, previously recorded with the simpler batch-mode technique.[28]

2. Experimental Section

Chemicals. All the reagents used were of analytical grade and were employed while preventing any alteration to the quality guaranteed by the supplier (Merck). Only deionized water with specific conductivity below 1 μS cm^{-1}, provided by a Demiwa ROI water purification unit, was put to use for all operations, and stock solutions were always utilized no more than 48 h but no less than 12 h following their preparation.

H_2SO_4 supplied was standardized to primary standards of $(COOH)_2 \cdot 2H_2O$, employing titration with fresh carbonate-free NaOH solutions, serving as the secondary standards.[38] Only stabilizer-free H_2O_2 was used, and the actual concentrations of its stock solutions were determined before each experiment, following the routine procedures[38] of titration with secondary standards of $KMnO_4$, itself being simultaneously standardized to primary standards of $(COOH)_2 \cdot 2H_2O$.

KIO_3, acetone, and $MnSO_4$ used as the monohydrate were all assumed to be well-defined and stable substances; hence they were treated as primary standards, and the concentrations of their stock solutions were determined by simply weighing the solutes accurately.

Instrumentation. All the experiments regarded herein were conducted in the apparatus schematically demonstrated in Figure 1. Reactions take place in a well-thermostated cylindrical reaction vessel (Figure 1a) with 32−33 mm inner radius and approximately 50 mL total volume, made of standard laboratory borosilicate glass (Simax). The vessel, charged with 30 mL of reaction mixture and a 21 × 6 mm rodlike magnetic stir-bar, is fixed on a magnetic stirrer (Figure 1b) and fitted with a rubber stopper.

The stopper is equipped with two electrodes and two glass tubes. The saturated mercurosulfate reference electrode Monokrystaly RME 121 (Figure 1c) and the platinum indicator electrode Radelkis OP-0612P with approximately 0.4 cm^2 total surface (Figure 1d) are employed to follow the changes in composition of the reaction mixture potentiometrically, and the two glass tubes provide access to the gaseous components of the system. One of the tubes extends approximately halfway down the reaction vessel, leads to a straight bore stopcock (Figure 1e), and serves for introducing gases into the reaction vessel. The other tube just enters the vessel and extends to a T-bore three-way stopcock (Figure 1f), where one of the arms connects the apparatus with an aspirator through a safety gas-washing bottle, and the other leads to the detection compartment of the apparatus.

This consists of a 25 mL detection burette (Figure 1g) provided with a graduated scale and having the tip extended with a glass tube, so that it almost reaches the bottom of the 100 mL beaker (Figure 1h) filled with the detection liquid. This can be charged into the detection burette using the aspirator, great care being taken not to cause degassing of the liquids present, preferably even protecting the reaction mixture from the lowered pressure with the three-way stopcock. Using it to isolate the detection compartment, the aspirator was also employed for drying the glass tubing with a quick acetone wash and a current of air, before each measurement, to eliminate the interference of water drops sealing the tubes and moving inside them. On the other hand, the three-way stopcock was usually blocking the aspirator, when gas was introduced into the system through the straight bore stopcock, so that complete saturation of both the reaction mixture and the detection liquid is ensured.

The beaker (Figure 1h) is placed on the pan of the digital scale Axis AD200 (Figure 1i), and so the changes in the amount of detection liquid in the detection burette are reflected in data obtained from the scale. The signal, as well as the signal from the digital multimeter Metex M-4660A (Figure 1j) measuring the potential difference between the electrodes (Figure 1c,d) were transmitted to the PC, where they were collected on the RS-232 serial port interface. Integration of the measuring devices with the software was achieved using the MSComm.ocx control (Microsoft), enabling us to easily record and evaluate the measurements in applications executed in the Visual Basic for Applications environment of Microsoft Excel.

Procedure. The initial composition of the BR reaction to be reproducibly measured in the apparatus proposed, as well as the reaction conditions, were adopted from the experiments referenced,[28] thus representing 0.1 M H_2SO_4, 0.4 M H_2O_2, 5.0 $\times 10^{-3}$ M $MnSO_4$, 0.035 M KIO_3, and 1.3 M acetone at 25 °C and under total exclusion of light. The stirring frequency was set to the highest intensity providing more or less uniform mixing of the reaction matrix, approximately 800 rpm.

The first set of experiments also maintained $MnSO_4$ as the final component of the mixture, initiating the reaction, as well as the presaturation of the system with the 900 s inflow of O_2, in our case approximately 10 mL s^{-1} strong. However, as the reports referenced[28] did not provide any justification for initiating the reaction with $MnSO_4$, a set of experiments intended to verify this choice also had to be performed. The next measurements were, therefore, conducted with the reaction mixtures prepared as in the first set, except for substituting the solution of $MnSO_4$ or KIO_3 for equal amounts of pure water and omitting the presaturation with O_2, thus roughly simulating the chemistry of the incomplete reaction matrix right from the point of its preparation.

The last set of experiments then restored the full composition of the reaction mixtures. This time, however, the reactions were initiated with KIO_3, and the system was not presaturated with O_2, even though the 900 s break period after its preparation has been maintained. Furthermore, prior to each experiment, the reaction vessel, the stir-bar, the electrodes, and the tubing of the apparatus were rinsed with the stock 5 M solution of H_2SO_4. A set of blank measurements, repeating the procedure outlined with pure water instead of the iodate stock solution, was finally recorded, too, and the measurements were evaluated.

3. Results and Discussion

As expected, completion of the reaction mixtures always caused its immediate change from colorless to orange-brown and was almost immediately accompanied by the evolution of gas. However, an unexpectedly broad spectrum of behavior was then observed to follow, especially in the first set of experiments, employing $MnSO_4$ to initiate the reactions and maintaining the presaturation of the reaction mixtures with O_2.

Though a few of the reaction mixtures completely failed to produce any oscillations at all, remaining in the state described, and producing gas at an almost constant rate of approximately 0.01 mL s^{-1}, most of the reaction matrices eventually began to oscillate. The overall shape of the potentiometric signal then recorded was clearly very similar to the signals reported previously,[28] indicating periodic alternation of the oxidized and the reduced phase of the reaction, and the patterns in the evolution of gas recorded in our setup at 800 rpm also corresponded to those measured by the simpler method[28] at 1000 rpm stirring. Each transition of the reaction mixture to the oxidized phase was followed by a burst of the gas production, peaking almost immediately at 0.03−0.05 mL s^{-1} and decreasing slowly, until almost no gas at all was produced in the following reduced phase of the reaction.

Nevertheless, many of the actual details of the overall course of the reactions were found to differ significantly - in comparison with the results previously reported,[28] as well as within the set of experiments itself. In the first place, the point of the first transition of the reaction mixture to the reduced state was initially found to vary quite randomly between 120 and 300 s, while gradually increasing and eventually even exceeding 1200−1300 s. Also the total number of oscillations generated, as well as the proportions between the durations of their two phases, differed and varied similarly, in part according to the time of the first transition of the reaction to the reduced state and partly in their own apparently haphazard fashion. Obviously, we had to draw the conclusion that even though our results showed to be consistent with the results obtained by the simpler method[28] (at least enough to consider the new method proposed as verified to be equally viable), the data measured were yet not sufficiently reproducible to be evaluated systematically.

Yet, having observed shifting of the whole oscillatory regime across the time axis in this set of experiments, we had also been led to another very important conclusion. Rather then considering the reaction to have no induction period and the oscillations to start and end with the transitions of the reaction mixture to the oxidized phase,[28] the orange-brown oxidized reaction phase producing gas should instead be considered to be the baseline state of the BR reaction with acetone, and its transitions to the reduced phases to represent the onsets of the oscillations. The peaks of the gas production rates should thus be located inside the respective periods of oscillations, even though this was particularly counterintuitive in the cases previously reported,[28] where the completion of the reaction matrix itself led to a similar peak at the beginning of the very first phase of the reaction, almost perfectly synchronized with the rest of the signal, which was, however, not the case in the results of the first set of these experiments.

One of the suspected possible sources of the discrepancies observed was, of course, the choice of the initiating reagent. This suspicion was proved justified by the results of the blank measurements, simulating the incomplete reaction matrices. Although the reaction mixture without KIO_3 produced no gas at all, the mixture without $MnSO_4$ (and with KIO_3) was found to slowly evolve gas at a rate gradually reaching a constant value of (6.6−7.4) $\times 10^{-4}$ mL s^{-1}.

This result clearly suggests that some reaction is taking place in the reaction mixture containing H_2O_2 and KIO_3, even before its completion with $MnSO_4$. Of course, this might largely be merely due to decomposition of H_2O_2, which could have just a negligible effect on its concentration. Nevertheless, other processes, potentially also producing some key intermediates of the BR reaction mechanism, might be taking place as well, especially as under specific conditions, H_2O_2 and KIO_3 in acidic medium themselves give rise to an oscillating reaction: the BL oscillator.[8,9] On the contrary, H_2O_2 in the incomplete reaction mixture does not seem to be similarly affected by the presence of $MnSO_4$ and therefore we had to draw the conclusion that employing KIO_3 instead of $MnSO_4$ as the initiating reagent could lead to enhanced reproducibility of the measurement.

The results of these gas-evolving blanks also made it possible to estimate the magnitude of the effects of the reaction mixture

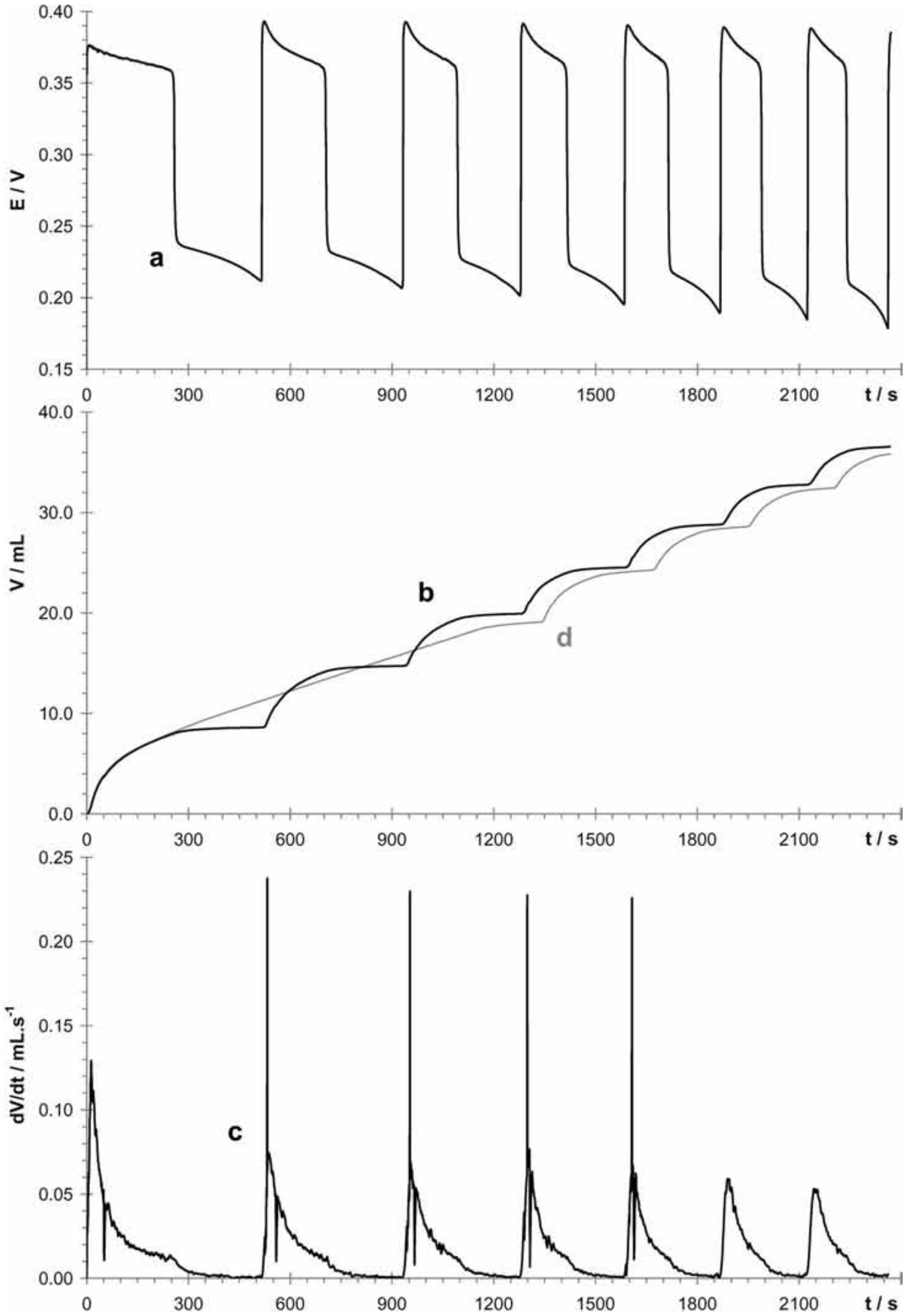

Figure 2. Potentiometric signal, volume of gas evolved and rate of evolution measured for the modified BR oscillating reaction. Initial composition: 1.00 M H_2SO_4, 0.40 M H_2O_2, 5.0 × 10^{-3} M $MnSO_4$, 0.035 M KIO_3, 1.30 M acetone. Reaction temperature: 25 °C. Reaction volume: 30 mL. Stirring rate: 800 rpm, conducted under exclusion of light. Reactions were initiated with KIO_3, 900 s after preparation, applying no prior saturation of the reaction mixture with O_2. Traces a−c represent a set of corresponding records obtained reproducibly, having adopted the procedure of treating all surfaces coming in contact with the reaction mixture with 5 M H_2SO_4 solution before each measurement. A typical measurement exhibiting the induction period, recorded under the same conditions as the trace b but before the reproducibility was attained, is represented by the trace of gas evolution (d).

presaturation on the measurement of gas production in the modified BR reaction. Assuming (quite roughly) the rate of the gas production to be constant right from the beginning of the measurement and the development recorded to be only due to gradual saturation of the reaction matrix, we approximated the volume of gas absorbed by the reaction mixture by calculating their difference. However, this represented merely approximately 0.1 mL, suggesting that the absorption of gas plays only a minor role in this case; therefore, we decided to eliminate the presaturation of the reaction mixtures with O_2 in the subsequent measurement as an unnecessary step, although the corresponding break period has been maintained to ensure thermal equilibrium of the system.

The actual correcting effect could be, however, explicitly demonstrated only in the case of the systematic error exhibited in the first set of measurement as the progressive increase of the reaction induction period. Because only a gradual accumulation of some insoluble reaction products or some other detrimental process on the surfaces in contact with the reaction seemed to be a likely cause of the additive effect observed, we decided to finalize the list of the adjustments proposed to the original experimental procedure[28] with washing of the reaction vessel, the electrodes, the stir-bar, and the tubing with the 5 M stock solution of H_2SO_4, prior to each reaction.

In the set of measurements conducted by adopting all the modifications outlined above, the induction period really began to gradually decrease, and after four runs it too has remained reproducible within the range 270−300 s. We were therefore led to the conclusion that the prior treatment of the surfaces in contact with the reaction mixture does substantially influence the reaction conditions, otherwise being gradually altered by the reaction mixtures themselves. Still, initiating the reaction with KIO_3 instead of $MnSO_4$ probably also eliminated a great source of other errors, as the results of the experiments really became more distinct and, most importantly, easily reproducible with our equipment. A typical set of records of the potentiometric signal, the total volume of gas produced, and the corresponding rate of production is displayed in Figure 2.

It is worth noting that although the length of the induction period on the potential signal (Figure 2a) is now again synchronized with the subsequent oscillations, its course is still slightly specific. This is, however, quite differently reflected in the total volume of gas produced and the rates of its production (Figure 2b,c); just when the rate of gas production previously used to become stable sometimes for as long as 1200 s, evolving gas at the rate of approximately 0.012 mL s^{-1} (Figure 2d), the first transition to the reduced phase now occurs. The gas thus seems to be evolved in evenly distributed bursts right from the very beginning, as inferred in previous reports.[28] The reduced phases should, nevertheless, still be regarded as the true initiators of the oscillations in the modified BR reaction, as it is their disappearance that causes the cycle to cease and the gas to again remain steadily evolved at approximately 0.01 mL s^{-1}.

The first periods of oscillation recorded, following the 270−300 s long induction periods, were 445−455 s long, with the reduced phases corresponding to approximately 60% of these values. Though the induction phases produced 8.63−8.98 mL gas, the first periods produced only 6.37−6.62 mL. Moreover, as the period of oscillation gradually decreased to 240−250 s after 2400 s of reaction, and the reduced and the oxidized phase became almost equal in length, the amount of gas evolved in each individual burst in the middle of the respective periods of oscillation attained a nearly constant value of 3.47−3.52 mL.

Interestingly enough, almost equal values of these parameters were determined even in all the first four runs of this set of experiments, despite the fact that in these cases the oscillations started much later, as illustrated by traces b and d in Figures 2. This tendency most likely points to the presence of a limit cycle of the oscillations, which appears to evolve in the system more or less independently from the mechanism creating individual oscillations.

The fact that emergence of the oscillations probably involves reactive species otherwise absent in the reaction matrix, whereas the parameters of the limit cycle depend mainly on the species present in large excess, is also supported by the average rates of gas production during the oscillatory domain of the reaction. On the levels around 0.016−0.017 mL s^{-1}, they are approximately 30% higher than the baseline values of 0.010−0.012 mL s^{-1}, even though more than half of the oscillatory period usually corresponds to the phases of the reaction, when the gas is not produced at all. However, as is obvious from Figure 2c, these phases are more than compensated by the vigorous evolution of gas observed after the transitions of the reaction back to the oxidized phase.

Furthermore, the figure documents that the precision of the experimental method employed also made it possible to record that the corresponding peaks of the gas evolution rate have a clearly reproducible structure. This usually seems to consist of a short stage of a very intensive initial evolution and a stage of a more gradual decline of activity, separated by a small but evident "crack" in the signal, which was not observed in blank recordings of approximately equal gas bursts introduced into the apparatus externally. In addition, this crack structure was found to gradually move toward the beginnings of the peaks, at a certain point even completely disappearing together with the most intensive stage of gas evolution, leaving behind only the more gradual phase.

At this point, however, we were not able to definitely conclude whether these two stages represent two distinct channels of the gas production, e.g., the first induced by the intermediates remaining after the transition of the reaction to the oxidized phase and the second brought along by their less reactive products, or the crack observed originates in the nonlinear dynamics of the gas nucleation.[9,10] Nevertheless, we found it absolutely evident that our experimental methods not only led to the procedures of measuring the modified BR reaction with enhanced reproducibility but also afforded experimental details that have not been reported previously.

Acknowledgment. This work was supported by Grant No. 1/3570/06 from the Scientific Grant Agency of ME SR.

Supporting Information Available: The procedure recommended for calibration of the apparatus proposed, as well as the corresponding protocol for correct evaluation of the experimental data acquired. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Scott, A. C. *The Nonlinear Universe*; Springer-Verlag: Berlin, 2007.
(2) Epstein, I. R.; Pojman, J. A. *An Introduction to Nonlinear Chemical Dynamics*; Oxford University Press: Oxford, 1998.
(3) Field, R.; Burger, M. *Oscillation and Traveling Waves in Chemical Systems*; Wiley-Interscience: New York, 1985.
(4) Noyes, R. M. *J. Phys. Chem.* **1990**, *94*, 4404.
(5) Zhabotinsky, A. M. *Biophysics* **1964**, *9*, 329.
(6) Degn, H. *Nature* **1967**, *213*, 589.
(7) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
(8) Bray, W. C.; Caulkins, A. L. *J. Am. Chem. Soc.* **1921**, *43*, 1626.
(9) Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 44.
(10) Briggs, T.; Rauscher, W. *J. Chem. Educ.* **1973**, *50*, 496.
(11) Volmer, M. *Kinetik der Phasenbildung*; Steinkopf: Leipzig, 1939.
(12) Smith, K. W.; Noyes, R. M. *J. Chem. Phys.* **1983**, *87*, 1520.
(13) Smith, K. W.; Noyes, R. M.; Bowers, P. G. *J. Phys. Chem.* **1983**, *87*, 1514.
(14) Dutt, A. K.; Menzinger, M. *J. Phys. Chem.* **1990**, *94*, 4867.
(15) Menzinger, M.; Jankowski, P. *J. Phys. Chem.* **1986**, *90*, 1217.
(16) Li, R. S.; Li., J. *Chem. Phys. Lett.* **1988**, *96*, 144.
(17) Ruoff, P.; Noyes, R. M. *J. Phys. Chem.* **1989**, *93*, 7394.
(18) Nagypal, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 6285.
(19) Menzinger, M.; Jankowski, P. *J. Phys. Chem.* **1990**, *94*, 4123.
(20) Ruoff, P. *J. Phys. Chem.* **1993**, *97*, 6405.
(21) Hlaváčová, J.; Ševčík, P. *J. Phys. Chem.* **1994**, *98*, 6304.
(22) Noszticzius, Z.; Bodnár, J.; Garamszegi, L.; Wittmann, M. *J. Phys. Chem. A* **1991**, *95*, 6575.
(23) Menzinger, M.; Jankowski, P. *J. Phys. Chem.* **1986**, *90*, 1217.
(24) Lopéz-Tomás, L.; Sagués, F. *J. Phys. Chem.* **1991**, *95*, 701.
(25) Pojman, J. A.; Dedeaux, H.; Fortenberry, D. *J. Phys. Chem.* **1992**, *96*, 7331.
(26) Valent, I.; Adamčíková, L'.; Ševčík, P. *J. Phys. Chem. A* **1998**, *102*, 7576.
(27) Ševčík, P.; Kissimonová, K.; Adamčíková, L'. *J. Phys. Chem. A* **2000**, *104*, 3958.
(28) Ševčík, P.; Kissimonová, K.; Adamčíková, L'. *J. Phys. Chem. A* **2003**, *107*, 1290.
(29) Ševčík, P.; Mišicák, D.; Adamčíková, L'. *J. Phys. Chem. A* **2007**, *111*, 10050.

(30) Onel, L.; Wittmann, M.; Pelle, K.; Noszticzius, Z.; Sciascia, L. *J. Phys. Chem. A* **2007**, *111*, 7805.

(31) Pelle, K.; Wittmann, M.; Lovrics, K.; Noszticzius, Z.; Turco Liveri, M. L.; Lombardo, R. *J. Phys. Chem. A* **2004**, *108*, 5377.

(32) Szabó, G.; Csavdári, A.; Onel, L.; Bourceanu, G.; Noszticzius, Z.; Wittmann, M. *J Phys. Chem. A* **2007**, *111*, 610.

(33) Noszticzius, Z.; Bódiss, J. *J. Am. Chem. Soc.* **1979**, *101*, 3177.

(34) Rachwalska, M. *Z. Naturforsch.* **2007**, *62a*, 41.

(35) Frattolillo, A. *Rev. Sci. Instrum.* **2006**, *77*, 045107.

(36) Dirckx, J. J. J.; Aernouts, J. E. F.; Aerts, J. R. M. *Rev. Sci. Instrum.* **2007**, *78*, 054705.

(37) Davis, D. D.; Stevenson, K. L. *J. Chem. Educ.* **1997**, *54*, 395.

(38) Vogel, A. I. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman Scientific & Technical: Harlow, 1989.

JP809969E