Temperature Compensation in the Oscillatory Bray Reaction

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The influence of temperature on the oscillatory frequency of the hydrogen peroxide−iodate ion reaction is found to be two-sided: (i) the period length decreases with increasing temperature in most of the instances studied, (ii) or in some cases an opposite change is observed. A temperature-independent period length (temperature compensation) is also discovered experimentally in a rather wide temperature interval at a narrow concentration range of reactants both in a batch configuration and under flow conditions. A simple model was considered to simulate this behavior. Opposing effects of the composite reactions of the model on the calculated period length with changing temperature are shown to be responsible for temperature compensation or overcompensation.

Introduction

A rise in temperature accelerates elementary steps of a chemical reaction, resulting generally in an increase in the overall rate. If such a rate increase takes place in the composite reactions of an oscillatory chemical system, one may expect that the characteristic period length becomes shorter because everything happens faster at elevated temperature. Indeed, a decreasing period length with increasing temperature is normally observed in most of the experiments.[1−7] Theoretically, however, a temperature-independent period or even an opposite dependence (increasing period length with increasing temperature) may also be possible in an oscillatory reaction network system, because such a system contains positive and negative feedback loops responding in opposite directions to the same temperature changes.[8−11] According to this theory, an increase of the rate constants belonging to the positive feedback reactions decreases the period length of an oscillatory system, while a similar increase in the rate constant values of the negative feedback reactions causes just the opposite change in the period length. In such a way, for a certain set of activation energies of the composite reactions, positive and negative feedback loops may tend to balance the influence of temperature on each other, leading to a temperature-independent period length. This phenomenon is called temperature compensation, which appears to be an essential feature of some biological rhythms. However, such a behavior stands in marked contrast to that found in most of the chemical oscillators, which are highly dependent on temperature. Despite significant effort, the first experimental example of temperature compensation in chemical oscillators has been reported in the hydrogen peroxide−thiosulfate−sulfite flow oscillatory system (CSTR) just recently.[12,13] In a closed chemical system, where the oscillations become generally more sensitive toward environmental changes, no temperature compensation has yet been reported, at all. In this work we show that the period length of the oscillatory decomposition of hydrogen peroxide in an aqueous solution containing acidic potassium iodate (the classical Bray reaction) may be independent of temperature under appropriately chosen experimental conditions both in a CSTR and in a closed vessel.

A few hints about the temperature dependence of the dynamical behavior of the Bray reaction are found in several papers.[14−18] Similarly to other oscillators, mainly a shorter period length has been observed at higher temperatures. In his original paper, for example, Bray reported an oscillatory period of about 4 days at room temperature and a few minutes at 60 °C.[14] Recently, however, Lanova and Vrestal[18] measured just the opposite dependence in an argon atmosphere at somewhat different conditions: they recorded a longer oscillatory period at 60 °C than at 50 °C and measured the shortest period at 40 °C. They determined some kind of “activation energies” from the value of the tangent of the dependence of $\ln(1/f) = F(1/T)$, where f is the oscillatory frequency ($1/f =$ period length). We think, however, that this treatment is not correct, because $1/f$ can be regarded neither as a real nor as an apparent rate constant, so the Arrhenius equation cannot be applied in such a way. Long ago, Körös[1] suggested similar use of the Arrhenius equation for calculation of the “apparent activation energy” of a chemical oscillatory reaction, but he plotted the logarithm of the frequency (not $1/f$!) as a function of $1/T$. If one applies Körös’ method for Lanova’s results in its original form, one obtains a negative value for the “activation energy”, which has no physical meaning. To characterize the temperature dependency of the oscillatory frequency, it is better to use the Q_{10} value, which describes the relative change in the period length when the temperature is increased by 10 °C. This parameter is frequently used for characterizing the temperature dependence of biological rhythms. It is defined as follows:

$$Q_{10} = (\text{period length at } T\ (°\text{C}))/(\text{period length at } T + 10\ (°\text{C}))$$

Q_{10} can also be given for a temperature interval T_1−T_2 not exactly separated by 10 °C:[6]

$$Q_{10} = (P_1/P_2)^{10/(T_2-T_1)}$$

where P_1 and P_2 are the period lengths in seconds at T_1 and T_2, respectively. A systematic experimental investigation of the

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effect of temperature on the oscillatory period length of the Bray reaction has not been reported yet. Here we carried out such a work and report our results. We found that, depending on the initial concentrations of the reagents, the measured period length might decrease with increasing temperature or could be independent of temperature in other cases or even an increase in period length might be observed as a function of increasing temperature. Simulation calculations using a simple model have also been carried out. The rate constants of the composite reactions of the model have been modified either individually or all together to simulate the effect of temperature changes.

Experimental Section

Materials. Reagent grade H_2O_2, $HClO_4$, and KIO_3 were obtained from REANAL and were used without further purification. Doubly distilled water used in preparing solutions was first purged with N_2 for the elimination of dissolved O_2 and CO_2. Stock solutions of H_2O_2 were prepared daily, and their concentrations were determined by titration with standard permanganate solution.

Reactor. Closed system experiments were carried out in a cylindrical-shaped, double-jacketed glass reactor with a liquid volume of 100 mL. This reactor was closed to the atmosphere. The continuous flow (CSTR) experiments were performed in a water-jacketed cylindrical-shaped glass vessel with a liquid volume of 12.5 mL. Thermostated water was circulated in the jacket of both reactors. The reactors were covered with a plastic cap in all the experiments. A Pt−Ag/AgCl combination redox electrode, a temperature probe, and the input (i.d. 1.0 mm) and output Teflon tubes (i.d. 2.0 mm) were led through the cap. A Teflon-covered magnetic stirrer bar (1.0 cm long) was used to ensure uniform mixing at around 500 rpm.

Procedure. Both the batch and the CSTR measurements were carried out in independent series of experiments performed at different temperatures. The uncertainty in controlling the temperature was ±0.05 °C. Concentrations of reagents were varied systematically one by one. The introduction of hydrogen peroxide stock solution to the heated mixture of potassium iodate and perchloric acid was taken as the initial moment of the reaction in the batch configuration. During the flow experiments, the CSTR was fed with input solutions of acidic potassium iodate and hydrogen peroxide by means of a peristaltic pump (Gilson). Two feedstreams enter the CSTR through two separated ports. Excess liquid was removed with the same pump. The temporal course of the reaction was followed by measuring the change in the redox potential. Potential−time data were collected by a computer and were recorded on a disk.

Results and Discussion

Batch Experiments. The Bray reaction is usually studied in an aqueous solution containing sulfuric acid. However, we used perchloric acid instead of sulfuric acid in most of our study, because preliminary experiments showed that the temperature range of oscillations became wider in the presence of perchloric acid. Note that $KClO_4$ did not precipitate in the concentration range we applied. A wider temperature range of oscillation is obviously an advantage when the effect of temperature on the dynamical behavior is studied in such systems. In a typical experiment, temporal oscillations started after an early preoscillatory (induction) period. Longer induction periods could be measured at lower temperatures in all the experiments. However, we found that the variation of the period length of oscillations with temperature is not so unambiguous. Typical oscillatory time series measured at different temperatures are shown in Figure 1.

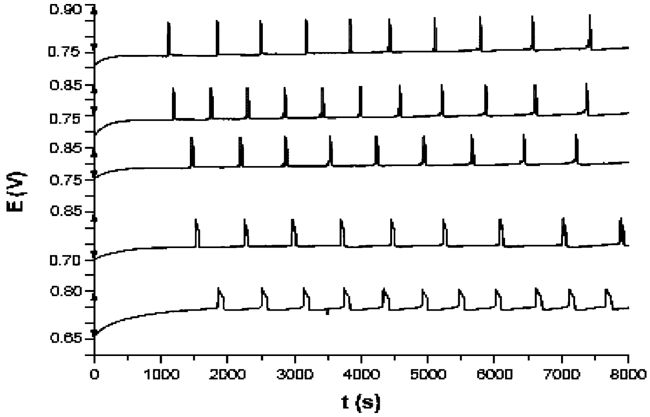

Figure 1. Oscillatory changes of the Pt electrode potential as a function of time in the Bray reaction in a batch reactor at different temperatures. $[H_2O_2]_0 = 0.1953$ M, $[KIO_3]_0 = 0.050$ M, and $[HClO_4]_0 = 0.055$ M. Temperature from the bottom to the top: 50.2, 55.8, 61.0, 65.2, and 70.2 °C. Period length from the bottom to the top: 9.63, 13.52, 12.47, 10.29, and 12.20 min.

TABLE 1: Reproducibility of the Period Length Measurements in a Temperature-Compensated Bray Reaction in a Closed Reactor[a]

T (°C)	65.5	70.0	75.0	80.0
period length (min)	1.49 ± 0.08	1.47 ± 0.09	1.59 ± 0.07	1.54 ± 0.09
number of measurements	3	3	3	3

[a] $[H_2O_2]_0 = 0.1953$ M, $[IO_3^-]_0 = 0.032$ M, and $[HClO_4]_0 = 0.10$ M.

It is seen in Figure 1 that the length of the preoscillatory period decreases and a gradual change in the shape of the oscillatory curves takes place as the temperature increases from the bottom to the top of Figure 1. Other experiments also confirm that the length of the preoscillatory period decreases with increasing temperature in all the cases studied. The period length of the oscillations, however, does not show any obvious trend as a function of temperature under the conditions shown in Figure 1. Note that the exact determination of the period length cannot be based on a single oscillatory period in a batch reactor, because any chemical oscillation is a transient phenomenon in a batch reactor: Sooner or later oscillations must cease as the reaction approaches equilibrium. Meanwhile the period length increases and the amplitude decreases in time as the reaction proceeds. In addition, the number of oscillatory cycles depends strongly on the initial experimental conditions. Consequently, under the circumstances, a single oscillatory period is not characteristic for a run. It is better, therefore, to calculate an average period length. Such an average value was calculated on the basis of the first 7−10 periods for each run throughout our study.

First, we looked at the reproducibility of the period length measurement because preliminary experiments indicated that significant deviation might arise in the simultaneously determined values. Shown in Table 1 are repeatedly measured period lengths at different temperatures.

Deviation from the average value observed in carefully repeated experiments can be kept below ±7%, which is acceptable in such measurements. On the other hand, the data in Table 1 indicate very good temperature compensation as the average of the determined period length remains within the reproducibility range in a temperature interval of 15 °C.

To determine the experimental conditions under which temperature compensation in period length appears, we per-

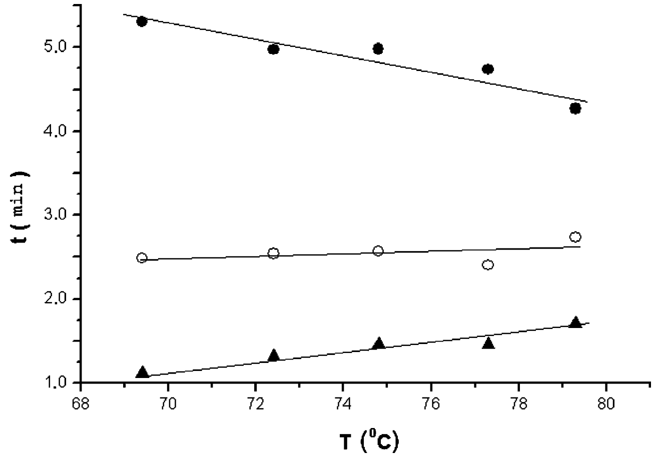

Figure 2. Measured period length (*t*) as a function of temperature (*T*) at different perchloric acid concentrations. $[H_2O_2]_0 = 0.10$ M, $[KIO_3]_0 = 0.08$ M, and $[HClO_4]_0 = 0.080$ (bottom), 0.070 (middle), and 0.060 (top) M.

TABLE 2: Experimentally Determined Q_{10} Values for the Bray Reaction in a Batch Reactor in the Temperature Range 69.3−79.3 °C at Different Reagent Concentrations

$[H_2O_2]$ (M)	$[HClO_4]$ (M)	$[KIO_3]$ (M)	Q_{10}
0.10	0.07	0.07	0.96
0.15	0.07	0.07	1.04
0.20	0.07	0.07	1.12
0.25	0.07	0.07	1.50
0.10	0.07	0.09	0.89
0.15	0.07	0.09	0.85
0.20	0.07	0.09	0.77
0.10	0.07	0.08	0.83
0.15	0.07	0.08	1.07
0.20	0.07	0.08	1.20
0.25	0.07	0.08	1.34
0.30	0.07	0.08	1.60
0.10	0.06	0.08	1.24
0.10	0.07	0.08	0.97
0.10	0.08	0.08	0.67
0.20	0.06	0.06	1.80
0.20	0.07	0.06	1.26
0.20	0.08	0.06	1.02

formed a series of experiments in a batch reactor, in which the reactant concentrations were varied systematically and the temperature dependence of the period length was measured. It turned out that both the direction and the size of the variation of the period length with changing temperature were very sensitive to both the initial concentrations of the reactants and that of the acid. Figure 2 shows the results of three series of experiments carried out at different concentrations of perchloric acid in a temperature range of 10 °C between 69.3 and 79.3 °C. One can observe a normal direction of temperature dependence at a 0.06 M $HClO_4$ concentration: the period length slightly decreases ($Q_{10} = 1.24$) with increasing temperature. At $[HClO_4] = 0.07$ M, good temperature compensation is seen, where Q_{10} appears to be close to 1.0 ($Q_{10} = 0.97$), while at $[HClO_4] = 0.08$ M, a reverse temperature dependence (overcompensation, $Q_{10} = 0.69$) can be measured.

Summarized in Table 2 are Q_{10} values obtained in the temperature range 69.3−79.3 °C at different initial concentrations of reagents and acid. Each Q_{10} value appearing in Table 2 is calculated as an average of three parallel experiments.

Our experiments revealed that the variation of the period length with temperature is not always monotonic. Shown in Figure 3 is a temperature−period length curve that shows a maximum.

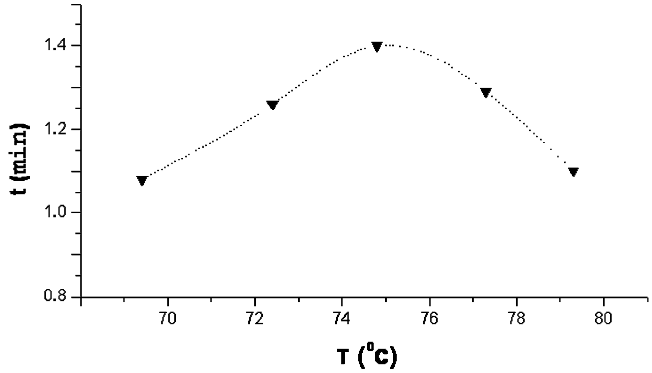

Figure 3. Measured period length at different temperatures in the Bray reaction. $[H_2O_2]_0 = 0.20$ M, $[HClO_4]_0 = 0.08$ M, and $[KIO_3]_0 = 0.060$ M.

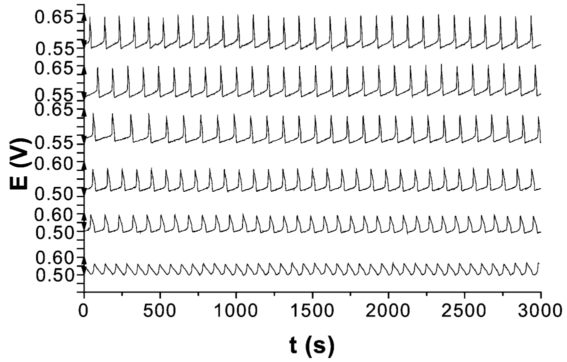

Figure 4. Oscillatory traces measured in a CSTR at different temperatures. $[H_2O_2]_0 = 0.1953$ M, $[KIO_3]_0 = 0.075$ M, $[HClO_4]_0 = 0.075$ M, and $k_0 = 4.7 \times 10^{-4}$ s^{-1}. Temperatures from the bottom to the top: 61.8, 65.2, 69.6, 75.0, 80.0, and 83.4 °C. Period length from the bottom to the top: 72, 88, 95, 105, 102, and 100 s.

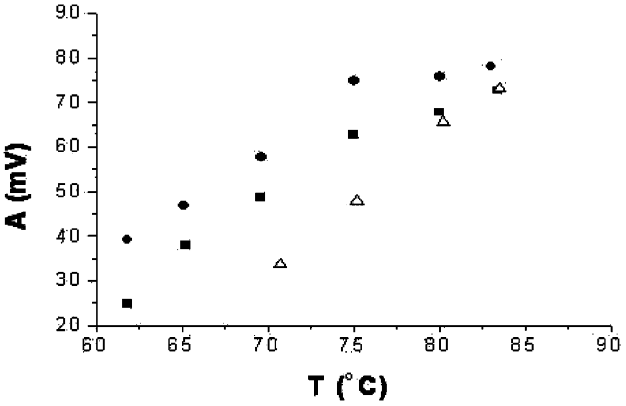

Figure 5. Measured amplitudes of temperature-compensated oscillations as a function of temperature in a CSTR. $k_0 = 4.7 \times 10^{-4}$ s^{-1}, $[H_2O_2]_0 = 0.1953$ M, (●) $[KIO_3]_0 = 0.048$ M and $[HClO_4]_0 = 0.075$ M, (■) $[KIO_3]_0 = 0.032$ M and $[HClO_4]_0 = 0.093$ M, and (△) $[KIO_3]_0 = 0.075$ M and $[HClO_4]_0 = 0.075$ M.

Experiments in a CSTR. Temperature compensation in the Bray reaction can be observed not only in a closed reactor but also in a continuous-flow stirred tank reactor. Figure 4 shows six oscillatory series measured in a CSTR in the temperature range 61.8−83.4 °C.

While the period length hardly changes with temperature (in the range 65.2−83.4 °C), the amplitude of the oscillations sharply increases with increasing temperature. The changes of amplitude of different temperature-compensated limit cycles are shown in Figure 5. The amplitude of these oscillations increases with increasing temperature, which is in good agreement with

TABLE 3: Composite Reactions, Rate Laws, and Rate Constants of the Bray Reaction[20]

$IO_3^- + I^- + 2H^+ \rightarrow HIO + HIO_2$	(R1)
$HIO + HIO_2 \rightarrow IO_3^- + I^- + 2H^+$	(R2)
$HIO_2 + I^- + H^+ \rightarrow I_2O + H_2O$	(R3)
$I_2O + H_2O \rightarrow 2HIO$	(R4)
$2HIO \rightarrow I_2O + H_2O$	(R5)
$HIO + I^- + H^+ \rightarrow I_2 + H_2O$	(R6)
$I_2 + H_2O \rightarrow HIO + I^- + H^+$	(R7)
$HIO + H_2O_2 \rightarrow I^- + H^+ + H_2O + O_2$	(R8)
$I_2O + H_2O_2 \rightarrow HIO + HIO_2$	(R9)
$HIO_2 + H_2O_2 \rightarrow IO_3^- + H^+ + H_2O$	(R10)
$IO_3^- + H^+ + H_2O_2 \rightarrow HIO_2 + O_2 + H^+$	(R11)
$I_2(aq) \rightarrow I_2(g)$	(R12)

rate law	rate constant at 60 °C
$v_1 = k_1[IO_3^-][I^-][H^+]^2$	$3.0 \times 10^3\ M^{-3}\,s^{-1}$
$v_2 = k_2[HIO][HIO_2]$	$1.32 \times 10^6\ M^{-1}\,s^{-1}$
$v_3 = k_3[HIO_2][I^-][H^+]$	$8.33 \times 10^9\ M^{-2}\,s^{-1}$
$v_4 = k_4[I_2O]$	$83.3\ s^{-1}$
$v_5 = k_5[HIO]^2$	$5.25 \times 10^6\ M^{-1}\,s^{-1}$
$v_6 = k_6[HIO][I^-][H^+]$	$1.0 \times 10^{12}\ M^{-2}\,s^{-1}$
$v_7 = k_7[I_2]$	$1.0 \times 10^3\ s^{-1}$
$v_8 = k_8[HIO][H_2O_2]$	$2.0 \times 10^2\ M^{-1}\,s^{-1}$
$v_9 = k_9[I_2O][H_2O_2]$	$3.33 \times 10^3\ M^{-1}\,s^{-1}$
$v_{10} = k_{10}[HIO_2][H_2O_2]$	$10.0\ M^{-1}\,s^{-1}$
$v_{11} = k_{11}[IO_3^-][H^+][H_2O_2]$	$1.87 \times 10^{-4}\ M^{-2}\,s^{-1}$
$v_{12} = k_{12}[I_2]$	$3.30 \times 10^{-4}\ s^{-1}$

the amplitude model proposed by Lakin-Thomas et al.[19] They predicted that, if a constant period occurs, the size of the limit cycle has to change. So increases of the environmental temperature increase the amplitude and decreases of the temperature have an opposite effect on the amplitude.

Modeling. In addition to the experiments, we have carried out model calculations to simulate the effect of temperature on the dynamical behavior of the Bray reaction. Obviously, an interesting question is whether the necessary mechanistic conditions of temperature compensation of the oscillatory frequency are fulfilled in the model[20,21] proposed for the Bray reaction in view of the fact that the rate of all the composite processes increases with increasing temperature. The model is shown in Table 3.

In Table 3 reaction R12 represents the evaporation of elementary iodine, which seems to be an important composite process with a significant effect on the period length when the reactor is open to air. No radicals are involved in the scheme. Obviously, the model is complicated, no analytical solution seems to be possible, and a numerical solution must be sought. A fourth-order Runge–Kutta method turned out to be appropriate for solving the model differential equations. The effect of a change in temperature on the period length may be simulated by changing the values of the rate constants. Simulations with two different sets of rate constants showed that a constant period length may be achieved if the values are chosen appropriately even if all the rate constants in one set are chosen to be higher than those in the other set. This is likely due to the opposing effect of the composite reactions on the period length.

In our simulations we demonstrate the existence of the opposing composite reactions in the reaction scheme R1–R11. In other words, our simulations show that there are composite reactions which increase the period length when their rate constants are increased and there are, on the other hand, composite reactions which decrease the period length when their rate constants are increased. It turned out that composite reactions R4, R6, R8, and R12 increase the period length when their rates are increased in the simulations, while reactions R1, R3, R5, R7, R9, and R11 have the opposite effect on the period length.

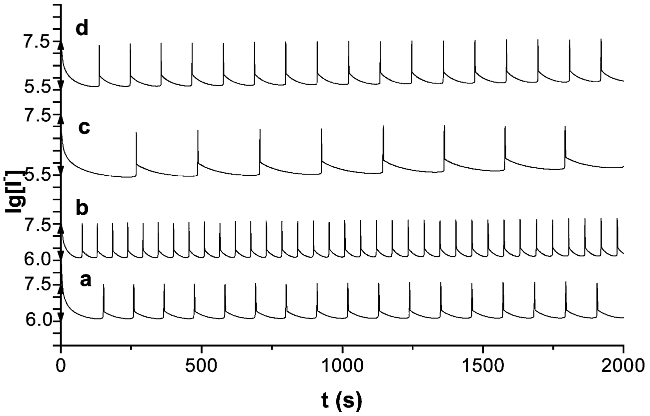

Figure 6. Calculated oscillations. $[H_2O_2]_0 = 0.20$ M, $[KIO_3]_0 = 0.036$ M, and $[HClO_4]_0 = 0.10$ M.

Shown in Figure 6 are temporal oscillations of the iodide ion concentration in a closed reactor calculated with different sets of rate constants. Curve a was obtained with the basic set listed in Table 3 assumed to refer to 60 °C. Then we doubled the rate constants of all the composite reactions. In such a way we tried to mimic the effect of a 10 °C temperature increase on the period length. As expected the period length decreased significantly (curve b in Figure 6). This means that temperature compensation cannot be simulated if the activation energies of the composite reactions are the same or very similar to each other. Curve c in Figure 6 was obtained when the rate constants of reactions R4, R6, and R8 were tripled, while other constants were doubled. Curve c shows clearly that, if reactions R4, R6, and R8 have higher activation energies than the other composite reactions, the period length will increase. Other simulations indicated that these three composite reactions not only together but also separately have such an effect. To simulate temperature compensation, we doubled the value of all the rate constants shown in Table 3, except $k_4 = 225\ s^{-1}$ and $k_8 = 520\ M^{-1}\ s^{-1}$. A comparison between curves a and d in Figure 6 gives theoretical evidence for the possibility of temperature compensation in the model and also shows an increase of the amplitude of temperature-compensated oscillation which has been observed in the experiments. Unfortunately, temperature dependence and activation energies of the steps in the mechanism are not known; therefore, more reliable simulations of the temperature compensation in the Bray reaction are not possible at the moment.

Conclusion

We observed temperature compensation of the oscillatory period length in the Bray reaction in a narrow concentration range of reactants both in a continuous-flow stirred tank reactor and under closed conditions. This experimental finding confirms Ruoff's theoretical considerations,[8] according to which a chemical oscillator can be temperature compensated under appropriate conditions because of the antagonistic balance between positive and negative feedbacks. We showed that an increasing rate of some composite reactions of a model proposed for the Bray reaction shortened the period length while an increase in the rate of other composite reactions has just the opposite effect. These two opposing effects compensate each other under a very limited range of conditions, resulting in a temperature-independent period length. We have also provided experimental evidence for Lakin–Thomas's theory,[19] according to which an increase in the temperature brings about an increasing amplitude of a temperature-compensated limit cycle oscillator.

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References and Notes

(1) Körös, E. *Nature* **1974**, *251*, 703.
(2) Blandamer, M. J.; Morris, S. H. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2319.
(3) Blandamer, M. J.; Roberts, D. L. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1056.
(4) Burger, M.; Körös, E. *J. Phys. Chem.* **1980**, *84*, 496.
(5) Kumpinsky, E.; Epstein, I. R. *J. Phys. Chem*. **1985**, *89*, 688.
(6) Nagy, G.; Körös, E.; Norunn, O.; Tjelflaat, K.; Ruoff, P. *Chem. Phys. Lett.* **1996**, *250*, 255.
(7) Kurin-Csörgei, K.; Nagy, G.; Körös, E. *Chem. Phys. Lett.* **1997**, *271*, 67.
(8) Ruoff, P. *J. Interdiscip. Cycle Res.* **1992**, *23*, 92.
(9) Ruoff, P. *Physica D* **1995**, *84*, 204.
(10) Ruoff, P.; Rensing, L. *J. Theor. Biol*. **1996**, *179*, 275.
(11) Valeur, K. L.; Agosti, R. D. *Biophys. Chem.* **2002**, *99*, 259.
(12) Rábai, G.; Hanazaki, I. *Chem. Commun*. **1999**, 1965.
(13) Kovács, K. M.; Rábai, G. *Phys. Chem. Chem. Phys*. **2002**, *4*, 5265.
(14) Bray, W. C. *J. Am. Chem. Soc*. **1921**, *43*, 1262.
(15) Peard, M. G.; Cullis C. F. *Trans. Faraday Soc*. **1951**, *47*, 616.
(16) Anic, S.; Stanisavljev, D.; Belovjev, G. K.; Kolar-Anic, Lj. *Ber. Bunsen-Ges. Phys. Chem*. **1989**, *93*, 488.
(17) Anic, S.; Kolar-Anic Lj.; Körös, E. *React. Kinet. Catal. Lett*. **1997**, *61*, 111.
(18) Lanova, B.; Vrestal, J. *J. Phys. Chem*. **2002**, *106*. 1228.
(19) Lakin-Thomas, P. L.; Brody, S.; Coté, G. G. *J. Biol. Rhythms* **1991**, *6*, 281.
(20) Kolar-Anic, Lj.; Misljenovic, Dj.; Anic, S.; Nicolis, G. *React. Kinet. Catal. Lett*. **1995**, *54*, 35.
(21) Kolar-Anic, Lj.; Schmitz, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2343.