

LIMIT CYCLE RELATIONS BETWEEN THE HEAT PRODUCTION RATE AND KEY INTERMEDIATE CONCENTRATIONS IN THE OSCILLATING BELOUSOV–ZHABOTINSKII AND BRIGGS–RAUSCHER REACTIONS

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ABSTRACT

Limit cycle relations between heat production rates and oscillating intermediate concentrations are obtained after deconvolution of the calorimetric signal. In the case of the Belousov–Zhabotinskii (BZ) reaction, the area of the power signal coincides for 60% with the fast, autocatalytic part of the process. Numerical simulation using the Oregonator model did not account for the heat production in the slow part of the process. The Briggs–Rauscher (BR) reaction shows a maximum in the heat production rate in the vicinity of the critical iodide concentration.

INTRODUCTION

The study of far-from-equilibrium phenomena, including oscillating chemical reactions [1], is now being given increasing attention. The underlying mechanism is the interplay of a coupled slow process and a fast, autocatalytic process. A powerful tool in the description of these phenomena is the use of the phase plane, in which the oscillating intermediates are represented by limit cycles. During the last 20 years, results on the heat production of oscillating chemical reactions have been reported [2–7]. However, a proper relation between the heat production and a key intermediate concentration has not been presented, as either deconvolution to compensate for the thermal inertia of the calorimeter has not been performed or a reference signal has not been measured.

In this paper, limit cycles between the bromide concentration, the Ce^{IV} concentration, the iodide concentration and the heat production rates are

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presented after dynamic correction of the calorimetric signal. As no simple reaction model has been developed for the Briggs–Rauscher (BR) reaction, numerical simulation was carried out for the Belousov–Zhabotinskii (BZ) reaction.

THEORETICAL

The power generated by a set of reactions is the sum of the reaction rates v multiplied by the reaction enthalpies ΔH

$$P = (dH/dt) = \sum_i v_i \Delta H_i \quad (1)$$

The power signal thus reflects the overall process in a chemical reaction system.

The signal obtained from a device is a convolution of the real physical event and an unwanted device-specific response. In general, the part of interest can be obtained by application of Fourier-transform deconvolution or by dynamic correction. In both cases, the device must be calibrated by studying its response to a well-defined input signal. In this paper, only dynamic correction is performed; the general application of (fast) Fourier transform deconvolution to periodic signals was described in ref. 8. Dynamic correction of a calorimetric output is obtained by

$$P = \alpha [\theta + (\tau_1 + \tau_2)(d\theta/dt) + \tau_1\tau_2(d^2\theta/dt^2)] \quad (2)$$

For a clear derivation of eqn. (2), the reader is referred to ref. 9. α is the heat-exchange coefficient, P represents the deconvoluted power signal, θ is the temperature difference between the calorimeter vessel and its surroundings, τ_1 is the first time constant, which is equal to the ratio of C_p and the exchange coefficient with an isothermal bath, and τ_2 is the second time constant and represents the inhomogeneity of the reaction vessel content.

EXPERIMENTAL

BZ reaction

A reaction vessel with an internal volume of 200 ml was equipped with an NTC thermistor (1 k Ω), a calibration resistor (50 Ω), an Hg|Hg₂SO₄ reference electrode (Radiometer type K601), a platinum wire with a diameter of 0.5 mm and a length of 10 mm, and a silver–silver bromide electrode with a diameter of 5 mm and a length of 10 mm. The last was made by coating a silver electrode with silver bromide by electrolysis in a 0.1 M KBr

solution for 2 min at an anodic current of 5 mA. A Nernst-like behaviour was observed between bromide concentrations of 10^{-1} M and 10^{-7} M and $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$ ratios between 10^{-6} and 1, although in 1 M sulfuric acid the normal potential of the reference electrode was found to be 0.1 V higher than its value in neutral solutions.

The NTC thermistor was incorporated into a Wheatstone bridge and, like the electrodes, connected to one of the channels of a Keithley 199 scanner–digital voltmeter. The bridge voltage and EMFs could successively be measured between well-defined time intervals by an Olivetti personal computer equipped with an IEEE bus.

The first and second time constants τ_1 and τ_2 were obtained by dissipating a known amount of electric energy in the system containing mixtures comparable with the composition of the reaction mixtures. The last three-quarters of the response signal was fitted to an exponential function, from which τ_1 was obtained. Consequently, this function was subtracted from the original signal and the difference was fitted to another exponential function which contains τ_2 . The reliability of the deconvolution method was controlled using square waves with various frequencies.

The reaction mixture was composed of 1.0 mM Ce^{III} -sulphate, 0.25 M malonic acid, 63 mM sodium bromate and 1 M sulfuric acid. All reagents were analytical grade. The volume was 100 ml and the reaction was started by the addition of cerium sulphate. During the experiments, the reaction vessel was immersed in a thermostatic bath at 25°C . The starting temperature of the mixture was adjusted so that within a few oscillations a temperature of 25.0°C was reached.

BR reaction

The conditions were as described above except for the following differences. As an attempt to measure Mn^{2+} had not been successful [9], the Pt electrode was removed. A silver–silver iodide electrode was used instead of the bromide analogue. It was prepared by coating a silver electrode with silver iodide by electrolysis in a 0.1 M KI solution for 5 min at an anodic current of 5 mA. Nernst's law was satisfied between iodide concentrations of 10^{-1} M and 10^{-6} M. The reaction was carried out in a mixture containing 6 mM MnSO_4 , 45 mM malonic acid, 60 mM sodium iodate and 25 mM sulfuric acid. The total volume was 100 ml.

The reaction was started by the addition of the MnSO_4 solution.

Numerical simulation

For a detailed description of the Oregonator reaction model and its mathematical treatment, the reader is referred to ref. 10. The Oregonator

reaction scheme is given by



In which $X \equiv \text{HBrO}_2$, $Y \equiv \text{Br}^-$, $Z \equiv \text{Ce}^{\text{IV}}$, $A \equiv \text{BrO}_3^-$, P and Q are waste products and f denotes a stoichiometric parameter.

Simulation was carried out by integrating the following equations

$$d\alpha/d\tau = s(\eta - \eta\alpha + \alpha - q\alpha^2) \quad (8)$$

$$d\eta/d\tau = (1/s)(-\eta - \eta\alpha - f\rho) \quad (9)$$

$$d\rho/d\tau = w(\alpha - \rho) \quad (10)$$

which contain only dimensionless variables and constants. α , η and ρ are related to the HBrO_2 concentration, the bromide concentration and the Ce^{IV} concentration, respectively. τ is the dimensionless time and s , w and q are dimensionless rate constants, which were calculated from the revised constants from ref. 11. The integration method was a Runge–Kutta technique and propagation of rounding errors was prevented by varying the increment. The heat production rate was computed by adding the reaction rates times the corresponding reaction enthalpies during the integration. The reaction enthalpies were chosen such that the experimental results were best approached. The calculation time on an Olivetti personal computer was about 20 min for one oscillation cycle.

RESULTS

BZ reaction

The experimental and simulated bulk intermediate concentrations and heat production rate versus time are presented in Figs. 1a and 1b, respectively.

The first and second time constants were 1×10^4 s and 7.6 s, respectively. An attempt was made to smooth the data using the noise reduction method of Savitzky and Golay [11,12], but this procedure revealed a highly deformed signal.

As expected from the reaction enthalpies [4] and the reaction rates [13] in this regime, the power signal maximum coincides with the fast, autocatalytic part of the reaction. The reaction enthalpy values adopted for simulation were 0.4 kJ mol^{-1} , 100 kJ mol^{-1} and 17.2 kJ mol^{-1} for the formation of

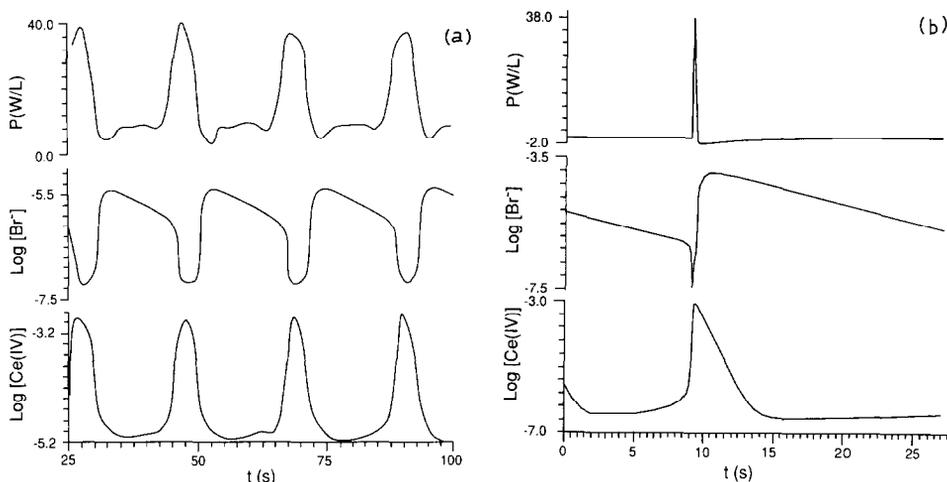


Fig. 1. Experimental (a) and simulated (b) $\log[\text{Br}^-]$, $\log[\text{Ce}^{\text{IV}}]$ and P versus time. All concentrations are in mol l^{-1} and the power is in W l^{-1} . In Fig. 1a, the time axis represents the time after addition of cerium sulphate.

intermediates represented by eqns. (8), (9) and (10), respectively. The major difference between experiment and simulation is the heat production rate during the slow part of the process, which is probably caused by slow following reactions. Obviously, the heat released during the increase of Ce^{IV} and the decrease of Br^- is much higher than that during the increase in HBrO_2 in this model. Figure 2 shows the experimental and simulated limit cycles in the $\log[\text{Br}^-]/P$ and the $\log[\text{Ce}^{\text{IV}}]/P$ phase plane, respectively.

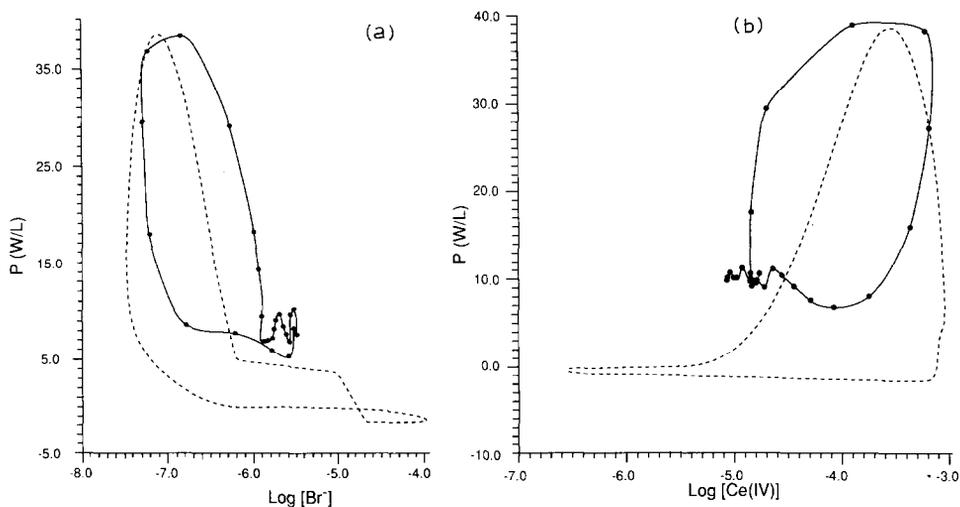


Fig. 2. Limit cycle trajectories of (a) the power P versus $\log[\text{Br}^-]$ and (b) the power P versus $\log[\text{Ce}^{\text{IV}}]$. The distance between the indicated points represents a time interval of 1 s. Concentrations are in mol l^{-1} , power is in W l^{-1} . Simulation is indicated by dashed lines.

To plot two variables in a phase plane it is necessary to know them both at the same time. Therefore, one of the signals was interpolated using cubic splines. This method proved to be valid in the error range of the potentiometric signals. The experimental trajectories were passed through for more than 10 oscillations. It is plausible to assume that in this range the concentrations of the reactants do not alter significantly, a situation roughly comparable with that in a CSTR (continuous flow well-stirred tank reactor), in which the concentrations of reactants are maintained constant. This condition is assumed implicitly in the Oregonator model. The difference between the experimental and calculated limit cycle is very large in the $\log[\text{Ce}^{\text{IV}}]/P$ plane, which is almost certainly caused by the fact that in the Oregonator model two reactions in which cerium is involved are taken together as one irreversible step [10,13], which is not a very fortunate approximation in this application. The agreement is much better in the $\log[\text{Br}^-]/P$ plane, and it is surprising that such a simple reaction model can qualitatively account for a complicated overall effect.

BR reaction

Figure 3 shows the deconvoluted power signal and the bulk iodide concentration versus time. Obviously, the power signal appears in the vicinity of the critical iodide concentration, i.e. the iodide concentration at which the process shifts from the slow to the fast regime. Comparison with the time derivative of some intermediates [14] reveals that the power signal resembles the iodine production rate. It may therefore be concluded that the

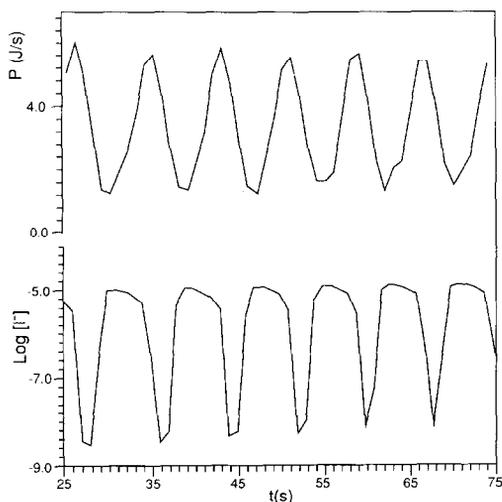


Fig. 3. Briggs-Rauscher reaction. Deconvoluted power signal (W l^{-1}) and bulk iodide concentration versus time after the start of the reaction.

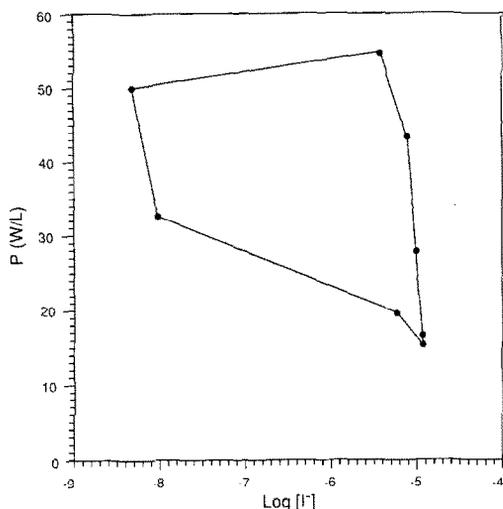


Fig. 4. Limit cycle trajectory of the power P versus $\log[I^-]$ in the Briggs-Rauscher reaction.

iodine production rate times its reaction enthalpy is a dominant factor in eqn. (1).

In Fig. 4, the limit cycle in the $\log[I^-]/P$ plane is presented. The indicated trajectory was followed for only a few oscillations, so that a CSTR-like situation as in the BZ reaction is rather questionable.

DISCUSSION

It has been shown that the relation between the heat production rate and comparable key intermediate concentrations, viz. the Br^- and the I^- concentrations, vary significantly with the oscillating reaction studied. The power signal is therefore an additional variable which contains valuable information on the overall process in an oscillating chemical reaction system. Certainly, the agreement between theoretical and experimental limit cycles will increase if a reaction model containing more variables is used. Experiments are in preparation in which the reactions are carried out in a CSTR in which the inflow of reactants can be varied.

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