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HEAT PRODUCTION IN OSCILLATING CHEMICAL REACTIONS: THREE EXAMPLES

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SUMMARY

Microcalorimetric measurements are reported for the metal-ion catalyzed Belousov-Zhabotinskii and the Briggs-Rauscher reactions as well as for the uncatalyzed reaction of phenol, bromate, and sulfuric acid. The rate of heat production and either optical or potentiometric signals are recorded simultaneously.

INTRODUCTION

Recently, a comprehensive survey on oscillations and travelling waves in chemical systems (ref. 1) has underlined the increasing interest in periodic chemical reactions since their modern establishment by Belousov (ref. 2) thirty years ago. All the reactions - studied so far - have been connected with a strong heat production and can thus be investigated by calorimetric methods. However, to date only a few oscillating systems have been analyzed by thermometry or calorimetry (see e.g. ref. 3-12). The calorimetrical approach is especially useful when combined with the simultaneous measurement of other physical signals (ref. 12). In this study we have concentrated on the simultaneous recording of the rate of heat production with that of either optical density or redox potential both of which facilitate the interpretation of the power time curves obtained.

Two types of oscillatory reactions were investigated: (1) metal-ion catalyzed reactions, such as the classical Belousov-Zhabotinskii reaction ("BZ reaction") (ref. 1-7,9,12) and the Briggs-Rauscher reaction ("BR reaction") (ref. 1,12,13); and (2) uncatalyzed reactions such as that observed on mixing phenol, bromate, and sulfuric acid (as an example of an "ABA reaction") (ref. 1,8,10,12-18).

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METHODS AND MATERIALS

Calorimetry

The experiments were performed using an isothermic, isoperibolic twin microcalorimeter type TRIFLUX (Thermanalyse/Grenoble) with stainless steel vessels of 1.2 ml, a sensitivity of 81.9 mV/W and a time constant of 117s. The calorimetric signal was amplified (type 150B Microvolt Ammeter, Keithley/München) and represented as a power time curve on a two channel recorder (type BD41, Kipp and Zonen/Kronberg). The reactions were started by adding one component of the recipe which was kept in a heat exchanger spiral during the time of thermal equilibration. Thereafter, the complete mixture was stirred continuously in the vessel throughout the experiment.

Photometry

The optical recording system simply consisted of a quartz light guide and a photo diode inserted into the calorimetric vessel. More details about the calorimeter and the integrative optical device can be found in (ref. 12).

Polarography

The polarographic recording system consisted of a platinum electrode dipping into the reaction vessel, a flexible salt-bridge to the top of the calorimeter and a calomel reference electrode (type 303, Ingold/Nürnberg). The signal was fed to the second channel of the recorder just as the optical one in other experiments.

Chemicals

All chemicals used were of analytical grade.

RESULTS

The thermodynamic characteristics of two catalyzed oscillating reactions (BZ and BR) and an uncatalyzed ABA system (phenol) were investigated. Fig. 1 shows the simultaneous records of temporal variations in the heat production rate and the optical density of the BZ reaction catalyzed by ferroin. This strongly exothermic (ref. 9) reaction consists of a catalytic oxidation and bromination of malonic acid. Phase relationships cannot be established directly from these graphs because the maxima of the power time curve are shifted due to the thermal inertia of the calorimeter.

For the second catalyzed oscillating reaction (the BR reaction (ref. 13), oscillations in the heat production and the redox potential are shown (Fig. 2). Some ten oscillations with a period of approximately 56 s are observed, before a strongly exothermic reaction connected with the precipitation of solid iodine breaks the oscillating state (ref. 12).

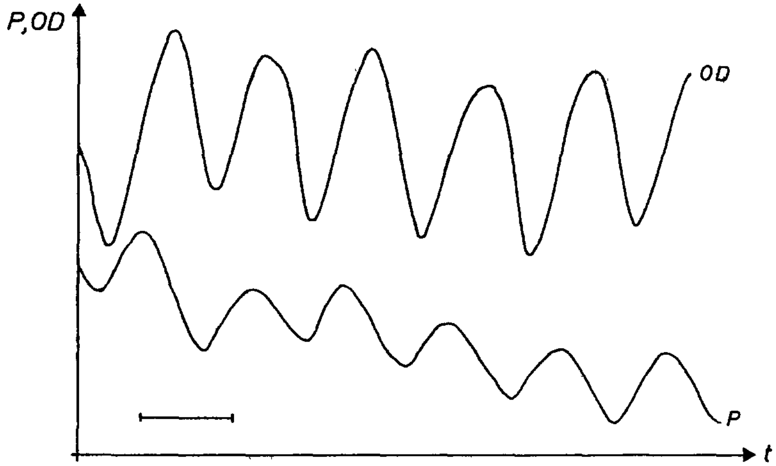

Fig. 1. Optical density OD and heat production rate P in the BZ reaction with the catalyst ferroin. The bar corresponds to 1 min, OD and P are given in arbitrary units.

As an example of an ABA reaction the heat production during the uncatalyzed oxidative bromination of phenol was determined. Fig. 3 shows a typical graph of the first part of such a reaction with a clear separation of the usual "preoscillatory period" (ref. 15) into a short endothermic part due to some diluting effects, followed by a weakly exothermic pre-period that led on to a strongly exothermic part, supposedly resulting from the formation of quinone and bromoderivatives (ref. 10). The area under the graph, corresponding to the heat produced during this period, is a linear function of the amount of phenol (Fig. 5). It renders a reaction enthalpy of -180.5 kJ/mol phenol which is close to the calculated value of -200 kJ/mol for the convertion of phenol to hydroquinone. During the preoscillatory period, not only is phenol consumed (ref.

15), but the first brominated derivatives also appear (ref. 15,17), so that some additional enthalpies have to be taken into account.

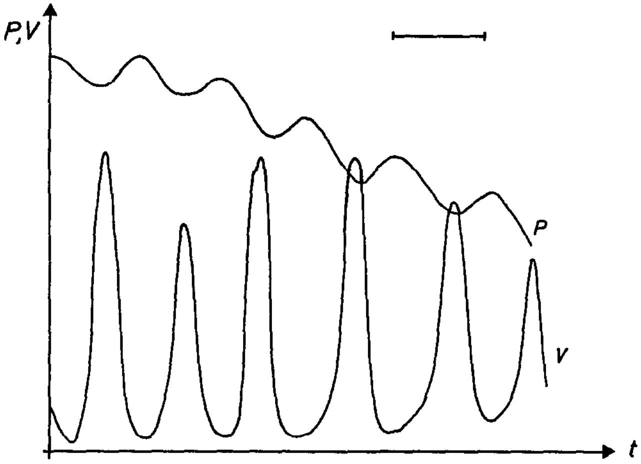

Fig. 2. Heat production rate P and redox potential V of a stirred BR reaction with the following initial concentrations: 25 mM potassium iodate; 0.9 M hydrogen peroxide; 30 mM malonic acid; 5.0 mM manganese(II)sulfate in 0.1 M sulfuric acid. The bar corresponds to 1 min; P and V are given in arbitrary units.

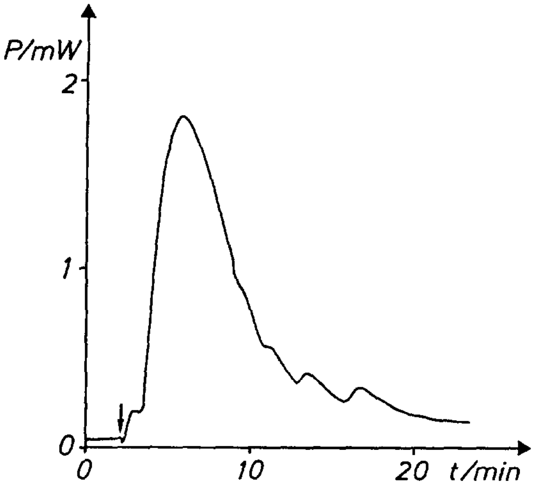

Fig. 3. Power time curve of a stirred ABA-phenol reaction at 25°C and 4 umol phenol. After thermal equilibration potassium bromate was added (arrow). A short endothermic phase followed by a pre-period and the main exothermic phase are visible and the first four oscillations on the falling slope of the curve.

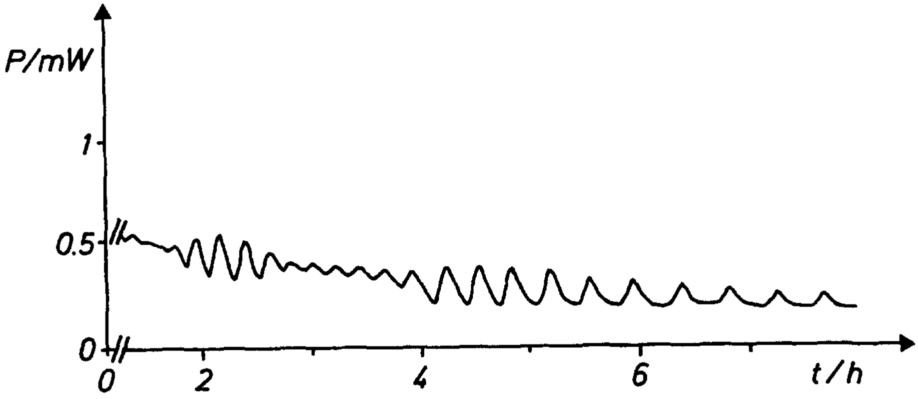

Fig. 4. Later part of the same experiment as in Fig. 3. In total 29 oscillations appeared which were modulated in their amplitudes.

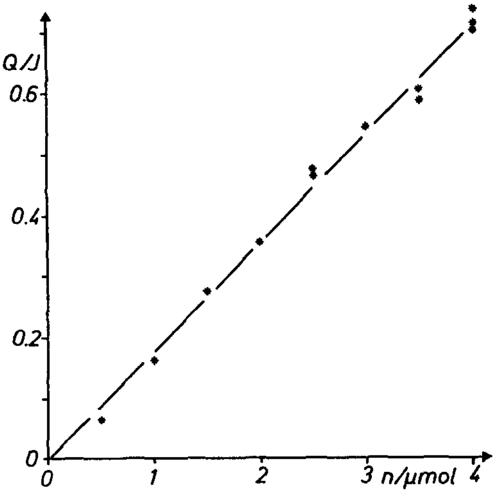

Fig. 5. Heat production Q during the first part of the ABA-phenol reaction as a function of the amount of phenol. The slope renders a figure of -180.5 kJ/mol phenol.

The length of the pre-period decreases strongly with increasing phenol concentration. The same holds good for the interval between the start of the reaction and the appearance of the first oscillation, which is usually situated in the falling slope of the graph (Fig. 3). One should note however that the true heat signal is 'smeared' by the thermal inertia of the calorimeter. Below a concentration of 0.5 µM phenol no oscillations could be detected. All these results fit well with the current view that only after the oxidation of part of the phenol are the conditions appropriate for the appearance of chemical oscillations (ref. 10).

The oscillations and intermittencies in a later part of such a power time curve are presented in Fig. 4. The number of oscillations increases with the amount of phenol but is sensitive to experimental conditions. Usually, the number of oscillations in an ABA system is much smaller than in catalyzed reactions such as the BZ one which can oscillate for up to days with only slowly decreasing amplitudes and increasing periods. Fig. 3 shows how the period increases from the first to the fourth oscillation in the ABA reaction.

Further conclusions concerning oscillatory heat production in relation to other periodic signals may be drawn after time consuming deconvolution computation of the calorimeter output.

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