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EXTENDED BATCH CALORIMETRY ON PERIODIC CHEMICAL REACTIONS

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SUMMARY

Three small setups for a batch microcalorimeter are described which allow for simultaneous determinations of the rate of heat production and of light absorbance, electrode potential or gas production. The setups are tested with fast chemical reactions and the time constants of the calorimetric signal have been determined thereby. Finally, examples are presented showing the usefulness of the device for investigations of periodic chemical reactions.

INTRODUCTION

In recent times chemical reactions with periodic time behaviour found increasing interest for studying phenomena far from thermodynamic equilibrium, for constructing kinetic models and computer simulations of such reactions and for developing mathematical approaches to the underlying problems. Periodic reactions have been measured by different methods, among them spectroscopy, chromatography, potentiometry and manometry (ref. 1). Although all oscillating systems studied so far showed a strong heat production (ref. 2-6), a fact realized by several authors, very few true calorimetric experiments were run on such systems (ref. 4,5,7-12). More often, thermistors or thermoelements were used to monitor temperature oscillations in closed batch systems or open continuous stirred tank reactors (CSTR). Sometimes, calorimetric or energetic data were drawn from such results (ref. 2) while in other cases just the fact of temperature as one periodic parameter among others was stated (ref. 13). In most experiments temperature fluctuations are small (0.01 to 0.1°C, while Franck and Geiseler (ref. 14) observed deviations of 1°C around a constant niveau for the bromination of malonic acid in the presence of a metalic catalysator (Belousov-Zhabotinskii (BZ) reaction). Bazsa and Epstein (ref. 15) reported temperature jumps of 1°C in travelling waves of the nitric acid-iron (II) system. In some investigations periodic temperature chan-

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ges could be measured together with changes in the redox potential or the concentration of a key substance of the oscillations (ref. 3,16).

Many recent investigations are run in isothermal tank reactors with continuous inflow of several constituents of the systems and an intensive stirring of the liquid (ref. 1,17,18). When the external parameters are set to appropriate values oscillations in light absorption, redox potential or specific concentrations can be observed for an indefinite number of periods in contrast to closed batch systems where the initially adjusted concentrations change with time and bring the oscillations to cease. As long as CSTR systems are not used in the sense of dynamic calorimetry (ref. 19, 20) with a continuous monitoring of the cooling rate to keep isothermal conditions, all information concerning energetics and periodic heat production are lost. Modern microcalorimeters with their small specimen size allow for isothermal investigations of oscillating reactions, but with the drawback of a closed system as in the experiments presented here in a batch manner. To overcome this disadvantage a CSTR may be coupled with a flow calorimeter; or the mixing cell of such an instrument can be taken as a CSTR if the system is reducable to two liquid streams. Such experiments with an LKB Flow Calorimeter will be published elsewhere.

Some reaction systems are known in which - usually at elevated temperatures - the temperature itself can be considered as an autocatalytic "substance" with a feed-back inhibition on the system (ref. 21). In such "thermokinetic reactions" the heat flow from the system to its surroundings is an integrative part of the mechanism of oscillations so that the emergence of the oscillations and their amplitudes can be influenced by the calorimetric set-up (ref. 22). Thermogenecity may be really high in such systems so that their temperatures change by more than 30°C periodically (ref. 6). On the other hand, in all reactions described below temperature oscillations appeared but played no role in the periodic kinetics.

Some periodic reactions not only exhibit temporal, but also spatial patterns (ref. 1). The best known example is the BZ reaction with travelling waves of different colours in flat containers (ref. 23-27). These impressive geometric structures are spatial inhomogeneities disturbing the calorimetric measurements. As calorimeters are integrating over the heat fluxes from all the volume elements of a specimen such inhomogeneities lead to a smoothing of the powertime-curves. As potentiometric electrodes and the absorption device presented below "see" just a very small part of the whole volume their graphs are much sharper and contain more details than the calorimetric results. To overcome this problem of sample inhomogeneities small specimens and an intensiv stirring of the calorimetric vessel are obligatory.

Calorimetry is often considerer to be a time consuming and slow technique. The relaxation time of the calorimetric signals amounts to one to two minutes, that of the redox potential to less than one minute. Such long relaxation times are disadvantageous when fast reactions or oscillating reactions with periods of a few minutes are studied. For some calorimeters the time response can be corrected sufficiently well by the Tian equation (ref. 28,29) which takes into consideration the first time derivative of the signal Fast Fourier Transform (ref. 30, this issue) offers a reasonable way to deal with longer relaxation times and to obtain the correct "desmeared" signal of the rate of heat production.

CALORIMETRIC CONFIGURATION

All the experiments described below were run with the isothermal isoperibolic twin calorimeter TRIFLUX (Thermanalyse/Grenoble) with stainless steel vessels of 1.2 ml and a sensitivity of 81.9 uV/mW. The signal was fed to a microvolt amplifier type 150B MICROVOLTAMMETER (Keithley/München), its 100 mV-output to a recorder and its 1 V-output to a 4-channel personal computer via an AD converter of 8 bit resolution. The digital data were stored for further analysis. Most experiments were run at room temperature, the chemicals used were of analytical grade.

For an easier comparison of calorimetric results with data from the literature and a deeper insight into the reaction mechanisms and kinetics three calorimetric insertions were developed for simultaneous determination of the optical density, the electrode potential and pressure changes which will be described to some details in the following chapters. These set-ups allow for a better analysis of the calorimetric signals and an assignment of heat production to special reaction steps.

A common feature for the three devices is that they fit through the calorimetric cover plate which carried a temperature equilibration coil. One component of the final reaction mixture was kept in this heat exchanger coil of 0.3 ml volume for an equilibration period and then pushed out by means of a syringe or sucked out by a partial vacuum to start the reaction. Immediately after the mixing a pneumatic stirring device could be connected to the calorimeter content via this exchanger coil.

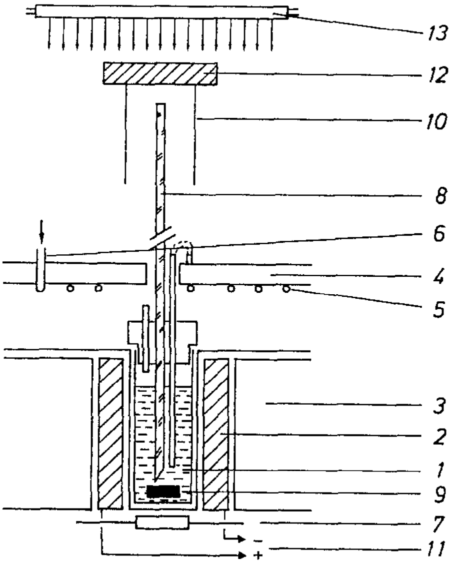

Fig. 1. Optical system to be inserted into the calorimeter for simultaneous determination of heat production and optical density. 1: calorimeter vessel; 2: heat flow meter; 3: thermostate; 4: cover plate of the calorimeter; 5: heat exchanger coil; 6: inlet to the coil; 7: calibration resistance; 8: quartz rod as light guide; 9: photo diode; 10: cylindric shield against stray light; 11: connection to the recorder; 12: interference filter; 13: fluorescent tube.

The optical-calorimetric set-up shown in Fig. 1 was described recently (ref. 11). Its main components are a quartz light guide, a photo diode and an appropriate fluorescent lamp as light source. A suitable wavelengths is selected by an interference filter. Further details of the construction are stated in the caption of Figure 1. The neutralization of 0.1 M HCl by an excess of 0.3 M NaOH was taken as a quick reaction. The optical signal was obtained by means of the pH indicator bromethymol blue (Fig. 2). The time constant of this set-up amounts to 117 sec.

The second set-up combines calorimetry with an electrode potential measurement (Fig. 3). The tip of a platinum electrode protudes into the liquid specimen, which is connected to an electrolyte reservoir on top of the calorimeter by means of a flexible salt

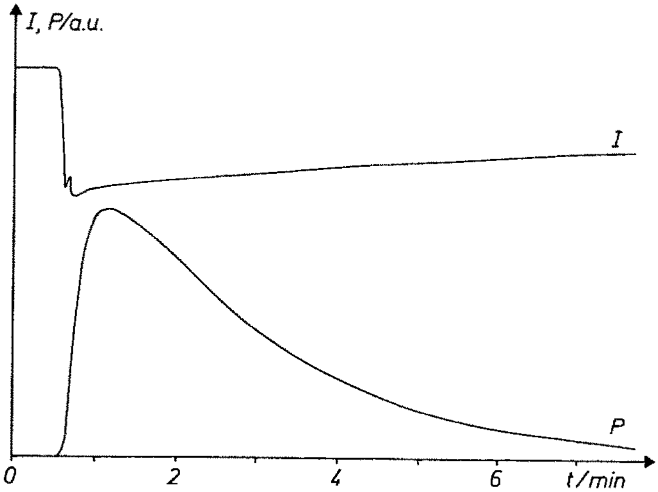

Fig. 2. Calibration curve for the optical device; neutralization of HCl with NaOH in the presence of a pH-indicator; I: optical signal, P: calorimetric signal. I and P are given in arbitrary units.

bridge. The potential is measured against a calomel reference electrode (type 303, Ingold/Nürnberg). Both signals are fed to a two-channel recorder or to the 4-channel PC. This device, calibrated with the neutralization reaction of HCl and NaOH (Fig. 4), is versatile in all those cases where the optical measurement is cumbersome due to the production of gas bubbles (Briggs-Rauscher reaction e.g.) or to not clearly defined spectra (some uncatalyzed bromination reactions). The oscillations in the potential amount to several hundred millivolts in all cases so that they can be recorded without any amplification. The time constant is a bit longer with 142 sec.

Many oscillating reactions are accompanied by a strong gas production (mainly carbon dioxide as in glycolysis, in the BZ and some ABA reactions or - together with oxygen - in the Briggs-Rauscher reaction; ref. 1,31). Therefore, it was worthwile to develop a pressure monitore. It consists of a semiconductor pressure transducer (NS 1602 G, National Semiconductors) connected to the free space above the reacting liquid by means of a capillary (Fig. 5). The transducer has an output of several hundred millivolts which are registered in the second channel of the recorder. The time constant of the calorimetric signal is 97 sec.

The easiest way to start such a pressure reaction is to produce

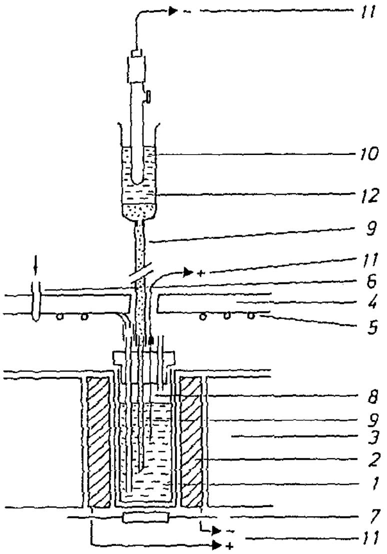

Fig. 3. Set-up for the simultaneous determination of the electrode potential. 1 to 7 as in Fig. 1; 8: platinum electrode; 9: salt bridge; 10: calomel electrode; 11: connections to the recorder; 12: reference solution.

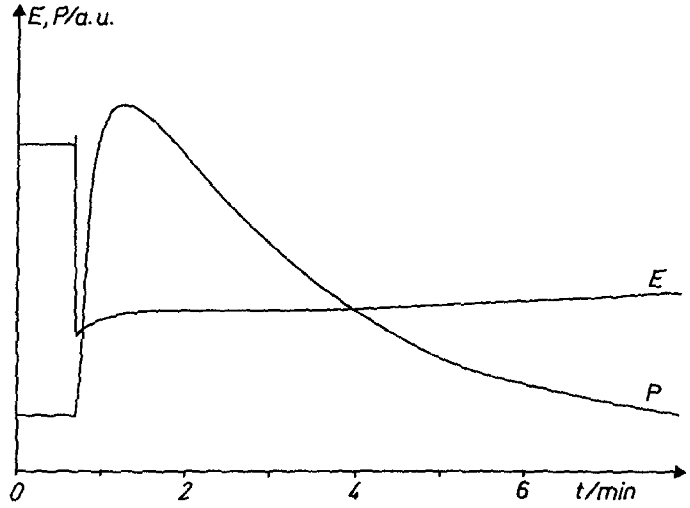

Fig. 4. Calibration curve for the potential device; neutralization of HCl with NaOH. E: potentiometric signal; P: calorimetric signal. E and P are given in arbitrary units.

a partial vacuum in the calorimetric vessel and to open the outside entrance of the heat exchanger coil for a short moment. The

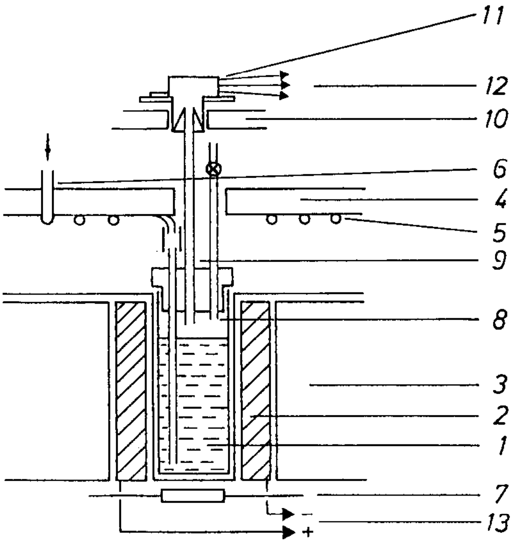

Fig. 5. Set-up for the simultaneous determination of the gas production. 1 to 7 as in Fig. 1; 8: canule for pressure equilibration and establishment of a low pressure; 9: connection to the pressure transducer; 10: support in the outside cover of the calorimeter; 11: pressure transducer; 12:, 13: connections to the recorder.

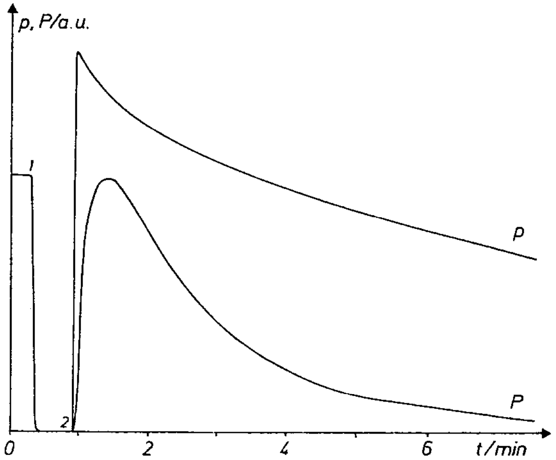

Fig. 6. Calibration curve for the pressure device; carbon dioxide production in the reaction of saturated sodium carbonate with diluted sulfuric acid. The partial vacuum was established at "1", the reaction started at "2". p: pressure signal; P: calorimetric signal. p and P are given in arbitrary units.

second constituent of the reaction is violently sucked into the vessel rendering a strong stirring effect. The pressure calibration curve (Fig. 6) was produced in this way by mixing a saturated sodium carbonate solution with diluted sulfuric acid rendering a strong carbon dioxide production.

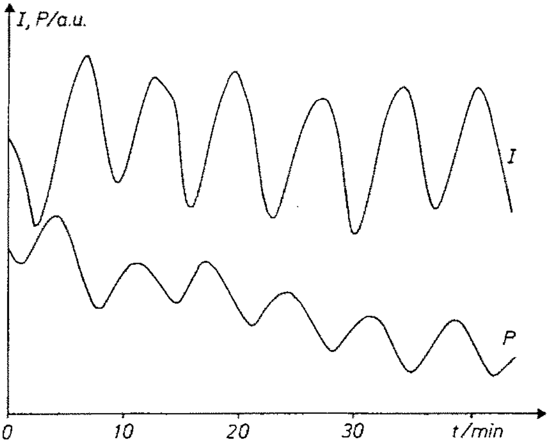

Fig. 7. Periodic structures in the heat production P and the optical density I of the BZ reaction. I and P are given in arbitrary units.

The oscillating gas production mentioned here has to be clearly distinguished from the so-called "gas evolution oscillators" (GEO) which depend upon supersaturation in the liquid (ref. 31). In the usual experiments on oscillating reactions an effective stirring of the liquid avoids supersaturation so that oscillating gas release is due to the periodic reaction itself and not to the physical effect of supersaturation. Sometimes it is advantageous in pressure experiments to incorporate a slow capillary leak to atmosphere so that the investigations run under nearly constant pressure.

Pressure measurements are not so straight-forward as the two other methods because liquids offer a solubility for gases and thus posses a strong buffering capacity. Pressure graphs are therefore less distinct than optical or potentiometric ones, but show a smoothed time resolution (ref. 32). Moreover, as they are integrative values, they just render a monoton stepwise increase of the signal and no true oscillations.

RESULTS

As this paper is mainly intended to introduce the new techniques for isothermal calorimetry, only a few results for the three methods will be presented below. One further example can be found in the paper of Müller and Plesser (ref. 30; this issue) which is based on the experiments performed with these devices.

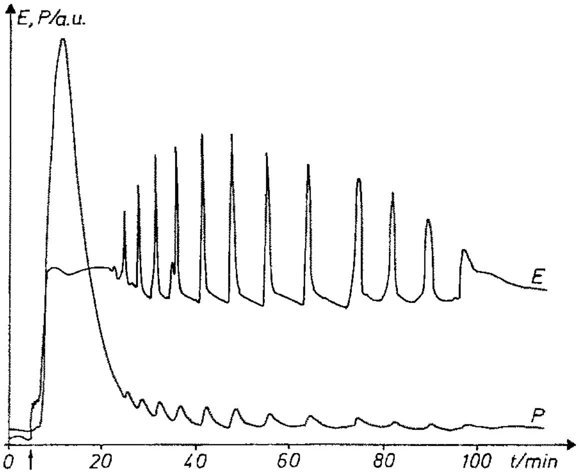

Fig. 8. Periodic structures in the heat production P and the electrode potential E of the bromination of phenol. E and P are given in arbitrary units.

The BZ reaction is known to be a strongly exothermic reaction (ref. 4) with intensive colour changes from red to blue if ferroin acts as catalysator and indicator. Fig. 7 shows the periodic changes in the rate of heat production and in the extinction at λ = 366 nm for this reaction. As known from the literature, the initially asymmetric curves change to more and more sinusoidal ones after a long duration of the experiment as seen here in Fig. 7.

Fig. 8 exhibits the simultaneous registration of the rate of heat production P and electrode potential E at the platinum electrode during the uncatalyzed bromination of phenol in the presence of potassium bromate and sulfuric acid (ABA reaction). After a short pre-period of a few minutes the main period starts with an oxidative bromination of the aromate to some chinone derivatives till the system enters the oscillating period characterized by two bromine controlled kinetic states. Usually, 6 to 12 oscillations are observed in the reaction which continues for a longer post-period with a low rate of heat production, but without further periodicity (ref. 12).

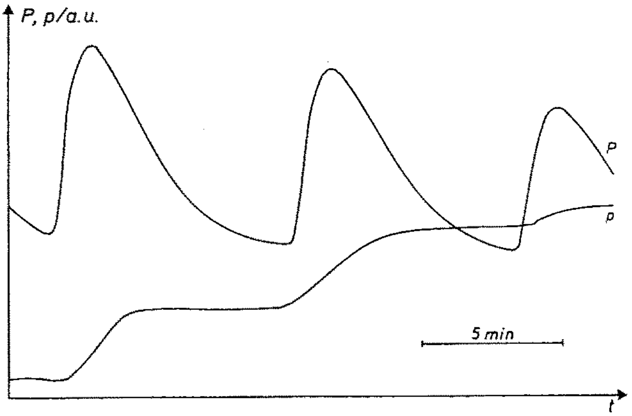

Fig. 9. Periodic structures in the rate of heat production P and the pressure increase p in the BZ reaction. p and P are given in arbitrary units.

In Fig. 9 the rate of heat production during three periods of the BZ reaction is compared with the stepwise increase of the pressure in the closed calorimetric system. One observes that the gas production coincides well with the part of the period with fast reaction and strong heat dissipation and that it is nearly zero during the second part of the period.

Fig. 10 demonstrates the effect of the Fast Fourier Transform on the calorimetric output. The lower graph shows the original heat signal before deconvolution, the upper one the graph after mathematical treatment. It becomes obvious that the heat production returns to the base line between the different heat "pulses", which are clearly separated in time. Only after such "desmearing" it is allowed to determine the heat output during a particular pulse because there are mutual interferences in the original calorimetric trace. More information about the procedure and the disturbances appearing in the deconvoluted graph is given in the paper of Müller and Plesser (ref. 30, this issue).

DISCUSSION

The literature survey and the few examples presented here underline that modern microcalorimetry is an interesting tool to study temporal patterns in chemical and biochemical reactions. Calorimetry complements other methods such as the determination of optical density, redox potentials or substrate concentrations. It renders energetical informations which can not be drawn from the other approaches and only to a first approximation from thermometry. It is the only method which allows for a continuous monitoring of the flux through the system. The other techniques complement this information by "snapshots" of the momentary situation of the reaction regarding concentrations, electrode potentials or optical densities. Thus calorimetry offers the unique chance to determine the energetic and material flows which meet the conditions necessary for the oscillatory window.

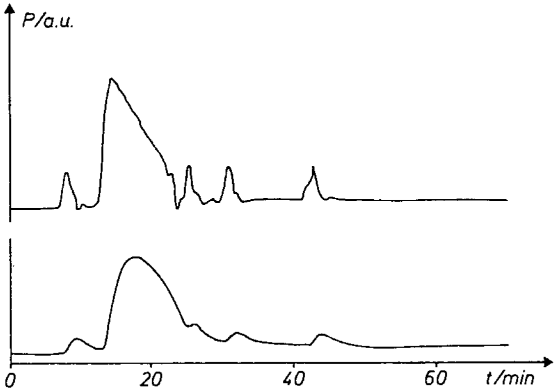

Fig. 10. Original calorimetric signal (lower trace) and signal after Fast Fourier Transform deconvolution (upper trace) of an uncatalyzed bromination reaction with phenol.

The closed batch system and the longer relaxation time as drawbacks of calorimetry can be overcome by an appropriate choice of the instrument and mathematical treatment of the results (ref. 28-30). Moreover, the sensitivity of modern calorimeters was significantly increased so that even small amounts of an oscillating system in the range of a few hundred microliters may be investigated.

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