# SIMULTANEOUS CALORIMETRIC AND POTENTIOMETRIC INVESTIGATIONS ON SOME UNCATALYZED BROMATE OSCILLATORS (UBOs)

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## Abstract

Simultaneous calorimetric and potentiometric/thermometric measurements were performed on three uncatalyzed bromate oscillators (UBOs) showing distinct temporal structures. The following UBOs were chosen: a) the gallic acid (3,4,5-trihydroxy benzoic acid)–bromate; b) the 1-hydroxy-4-[(1-hydroxy-2-methylamino)ethyl] benzene (HME)–bromate; and c) the 1,4-cyclohexanedione (CHD)–bromate system. Their oscillating reactions were monitored by an isoperibolic batch calorimeter of the Calvet-type at 20°C and with a quasi-adiabatic Dewar setup at room temperature, and in addition by platinum/calomel potentiometry and thermometry. Shape of the calorimetric curves, number and duration of the oscillations and their frequencies varied considerably between these three UBOs. The underlying chemical reaction schemes are discussed in connection with the energetic background.

**Keywords**: calorimetry, potentiometry, uncatalyzed bromate oscillators (UBOs)

## Introduction

Oscillatory chemical reactions have been in the focus of interest since the early seventies partly due to their uncommon temporal behaviour and partly their connection – at least phenomenologically – to periodic processes occurring at many levels of material organizations. Especially the Belousov-Zhabotinsky type (BZ) reactions – the catalytic oxidation and bromination of certain organic compounds (mostly aliphatic polycarboxilic acids and polyketones) by acidic bromate – have been studied rather thoroughly [1].

Of the large variety of experimental methods used to reveal the 'secrets' of temporal as well as spatial periodicities also calorimetry proved to be an informative one. The calorimetric results obtained contributed considerably to our better understanding of the thermochemistry of the BZ systems. It could be demonstrated that in oscillatory reactions the rate of heat production was periodic and the temperature rose in a stepwise manner, and these appeared synchronized with the concentration oscillations of the reaction intermediates.

On the caloric behaviour of catalyzed bromate oscillators many papers have been published, however, our knowledge about the uncatalyzed bromate oscillators (UBOs) in this respect is rather vague, in spite of a revived interest in such systems.

For, recently a number of papers have been published on the dynamic behaviour of some of these systems studied under batch as well as under flow conditions. Few authors made suggestions on the chemical mechanisms, published simplified mechanistic models that could rather well simulate the temporal course of the reactions [2–6].

Noticeable contributions have appeared on the calorimetric studies of a few UBOs. Already in very early papers on UBOs authors claimed that under quasi-adiabatic conditions the temperature of the reacting systems increased stepwise [7, 8], similarly as reported in the early seventieth with the catalyzed bromate oscillators [9].

In the late seventies Lamprecht *et al.* performed more detailed investigations on the thermal behaviour of BZ oscillatory systems [10] and later on UBOs containing phenol, sulfanilic acid, respectively, aniline as an organic substrate [11, 12]. A review paper by Lamprecht summarized the most important results in this field [13]. Recently Mukherjee *et al.* reported on the calorimetry of the gallic acid (GA)–bromate reacting system. They performed the experiments at different reactant concentrations and also in presence of a catalyst, and they were concerned with the chemistry of the reaction [14]. We are going to comment on this paper in the Discussion Part of our present communication.

In the last decade our main goals were a) to reveal the chemistry of UBOs, i.e. to identify the products and if possible also some of the intermediates of the bromate–organic substrate reactions, and b) to elucidate the chemical mechanisms of these reactions. Other authors' and our own investigations have revealed that the reactions between bromate and an organic substrate (which in most of the cases is a phenol- or an aniline-derivative) are of a rather complex nature and can not be described by a simple stoichiometry. For, in these redox reactions oxidation, bromination, oxidative bromination and under certain conditions also oxidative coupling reactions run parallel [15].

Considerable differences in the dynamic behaviour of the reacting systems have been found when a) a polyphenol (e.g., pyrogallol, gallic acid), b) a para-substituted phenol (e.g., $R$=an alkyl amino group), or c) a non-aromatic organic compound (e.g., 1,4-cyclohexanedione, CHI) were the organic component of an UBO [16–18].

These observations, and primarily the unexpected behaviour of CHD in its reaction with acid bromate prompted us to make a comparative calorimetric study on three UBOs: on the a) gallic acid (3,4,5-trihydroxy benzoic acid) – bromate; b) 1-hydroxy-4-[(1-hydroxy-2-methylamino)ethyl] benzene (HME) – bromate; and c) 1,4-cyclohexanedione (CHD) – bromate systems.

## Experimental

### Reagents

Potassium bromate, sulfuric acid, gallic acid and CHD used in the experiments were of analytical purity grade from Merck (Darmstadt, Germany). HME was of purissimum grade supplied by Chinoin Ltd. (Budapest, Hungary). The standard solutions were: 0.02 M gallic acid, 0.02 M HME, 0.2 M CHD, and 0.5 M $KBrO_3$, all in 1.0 M $H_2SO_4$.

*Methods*

Reactions were initiated by adding certain amount of potassium bromate solution to the solution of the organic substrate. The temporal course of the reaction was followed calorimetrically and in most of the cases also potentiometrically. The total volume of the reaction mixture was 5,10 or 30 ml depending on the type of the calorimeter used in the experiments. The potential change of the reacting system was monitored with a platinum electrode which was connected with an electrolyte reservoir on the top of the calorimeter via a salt/agar bridge, and calomel was used as a reference electrode.

*Calorimeters*

Two different batch calorimeters were used in the present investigations, the first a Calvet-type isoperibolic differential setup with 15 ml active volume, the second a quasi-adiabatic Dewar system of 100 ml. Since construction and performance of these instruments are rather different, they will be discussed separately in the following paragraphs.

*Isoperibolic twin calorimeter*

This differential heat-flow calorimeter (type Biocalorimeter B.C.P., Electronique Arion, France) contains two identical cylindrical vessels of 17 mm diameter and 80 mm height, one for the reaction, the other for the reference. They are connected through 2 times 2 thermoelectric piles ('Peltier elements') as heat flow sensors with a larger heat sink of aluminium. Depending upon the intended reaction the vessels are made from stainless steel, pyrex or perpex. The vessels are inserted into the calorimeter by a support which may carry further equipment such as stirring devices, electrodes, canules for introduction of gas flows, or glass spirals for temperature equilibration of liquids, which may be added to initiate the reaction or to alter its pathways.

The sensitivity of the instrument was determined by the Joule effect by means of an electric heater of known resistance and with variable electric currents. It amounted to 45.8 mV W$^{-1}$. In many experiments the calorimetric signal was strong enough to be recorded directly by a flat bed recorder (type L6512, Linseis/Selb, Germany). If not, the signal was amplified 1000 fold by a DC amplifier (type A3, Knick/Berlin, Germany) and fed to the same recorder. To guarantee a stable baseline over extended time periods this calorimeter was placed in a thermostatted room kept at 17±0.5°C. No baseline changes were detectable in the chosen experimental settings.

Since the heat output rate of an oscillating reaction significantly changes during one period and phase shifts between different local parts of the vessel would level off the oscillating calorimetric signals it is essential to guarantee a perfect homogeneity throughout the volume . This was obtained by a mechanical stirring device moving 5 horizontal plates up and down through the solution [13, 19].

The 1/e-time constant of the calorimeter amounted to 3.6 min so that a smearing of the signal occurred. This made the oscillations less pronounced in the calorimetric picture, but was of no importance as long as only heat quantities were concerned and nei-

ther true amplitudes nor phase relationships. If necessary a desmearing procedure could be applied either by means of the Tian equation or a Fast Fourier Transform [13, 20].

The B.C.P. calorimeter was designed for biological investigations at heat flow rates around 1 mW or below. Under such circumstances the instrument may be considered as isotherm since temperature fluctuations due to biological activities are about 4 m°C and thus negligible. At the present research on oscillating reactions short-term heat production rates between 200 and 300 mW are possible, inducing temperature differences between vessel and thermostat of more than 1°C. The calorimeter is no longer isotherm, with significant effects on the reaction kinetics and oscillation frequencies.

*Quasi-adiabatic Dewar system*

For additional measurements a second calorimetric device was run under normal laboratory conditions at room temperature. This setup consisted of a 100 ml Dewar vessel closed with a cork stopper and isolated by a polystyrene box of corresponding inner diameter. The content of the Dewar (30 ml solution) was magnetically stirred at usually 500 rpm to ensure full homogeneity of the liquid and good thermal contact to a 3.8 kΩ thermistor reaching into the solution. This sensor was connected to a thermometric Wheatstone bridge with variable amplification (type Temperaturmessgerät, Knauer/Berlin, Germany). Its basic temperature sensitivity amounted to 12.46 mV °C$^{-1}$ and could be amplified up to 128 fold. The time constant of the system was in the order of 50 s. The output was fed to a multichannel recorder (type BD101, Kipp&Zonen/Delft, The Netherlands). Typical amplification settings were '2' and '4'.

The calorimeter was calibrated electrically and chemically rendering a heat sensitivity of 4.06 J ml$^{-1}$ °C$^{-1}$. The heat loss to the environment was determined as a function of temperature difference between solution and ambiance and amounted to 66.8·10$^{-6}$ °C s$^{-1}$ or 0.272 mW ml$^{-1}$ at 25°C. This value is negligible compared with the high heat output of the oscillating reaction.

# Results

*The gallic acid–bromate system*

It is known from earlier communications that when gallic acid is oxidized with bromate in sulfuric acid solution after a short induction period – depending on the concentration of the reactants – 8 to 15 oscillations can be recorded. The redox potential and/or the bromide ion concentration oscillations are very strongly damped.

Calorimetric experiments performed under isothermal conditions and at different reactant concentrations have shown that early during reaction the rate of heat production was very high and during the oscillatory phase of the reaction periodicity in the rate of heat production was observable (Fig. 1). In case the calorimetric experiments were run under quasi-adiabatic conditions stepwise increase in temperature characterized the oscillatory phase of the chemical process (Fig. 2). Here, not only
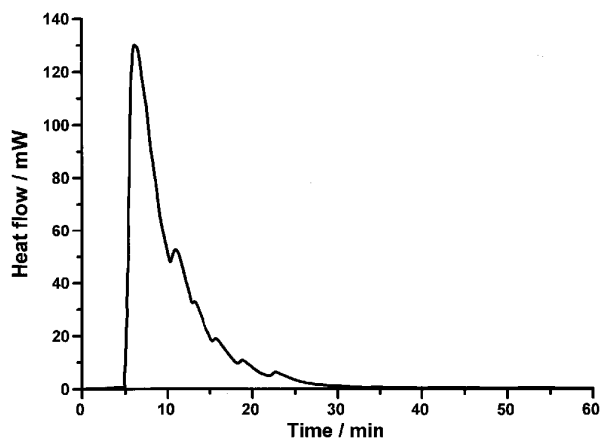
**Fig. 1** Rate of heat production in a gallic acid system; Initial concentrations: [GA]=0.018 M; [KBrO₃]=0.05 M; [H₂SO₄]=1.0 M; $t$=20 °C; $V_t$=5 ml; mechanical stirring

the temporal temperature change but also the temporal course of the redox potential have been followed. Recordings on Fig. 2 clearly show that the temperature jumps and the abrupt potential changes appear synchronized.

Under isothermal conditions also double-pen recordings were taken. In these experiments, however, magnetic stirring was replaced by bubbling nitrogen gas
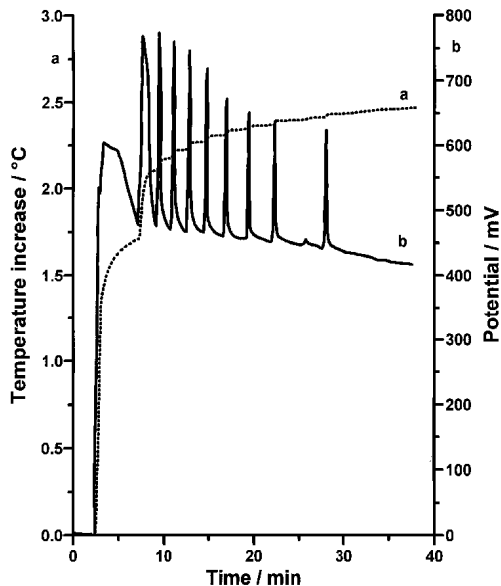


**Fig. 2** Temperature and redox potential changes in the gallic acid system under quasi-adiabatic conditions; Initial concentrations : [GA]=0.018 M; [KBrO₃]=0.05 M; [H₂SO₄]=1.0 M; room temperature; $V_t$=30 ml; magnetic stirring; a) Calorimetric trace; b) Potentiometric trace

through the solution. We observed that the main parameters of oscillations have changed in a non-negligible extent: the induction period and the period time of oscillations were longer and the amplitude of oscillations became higher than in the former experiments. This behaviour of the reacting system harmonized with the observations of Dutt and Menzinger [21], and will be discussed below.

**Table 1** Results of isoperibolic calorimetry on the oscillating gallic acid–bromate system: initial concentrations, duration of the preperiod (preper.), period time between the first and the second maximum (per. time) and number of oscillations (osc. number)

| [GA]/M | [KBrO$_3$]/M | Preper./min | Per. time 1–2/min | Osc. number |
|--------|--------------|-------------|-------------------|-------------|
| 0.018  | 0.05         | 4.5         | 3.6               | 5–7         |
| 0.01   | 0.05         |             | 7                 | 3           |
| 0.005  | 0.05         |             | 16.5              | 2           |
| 0.018  | 0.025        |             | does not oscillate |            |
| 0.018  | 0.03         | 5.4         | 26                | 4           |
| 0.018  | 0.04         | 5.4         | 12                | 4           |

Other conditions: [H$_2$SO$_4$]=1.0 M; Stirring rate=5 min$^{-1}$; $t$=20$^{\circ}$C; $V_t$=10 ml

Major parameters of the oscillatory system measured under different experimental conditions are compiled in Table 1. One of our experiments shows that below a threshold bromate concentration value oscillations do not set on. However, an additional amount of bromate mixed to the solution after 50 minutes resulted in the initiation of chemical oscillations (Fig. 3).

Figure 4 shows a simultaneous recording of the rate of heat production and the temperature change during an experiment, run in an isothermal calorimeter.

A few experiments were done at different stirring rates and we found that the higher the stirring rate was the longer were the induction period and. the period time
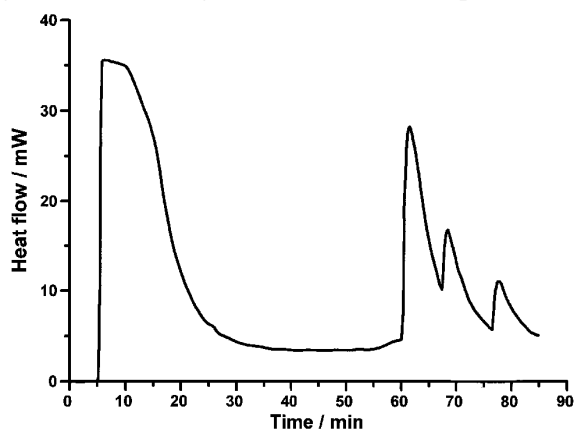


**Fig. 3** Initiation of chemical oscillations with an additional amount of bromate solution; Initial concentrations: [GA]=0.018 M; [KBrO$_3$]=0.025 M; [H$_2$SO$_4$]=1.0 M; $t$=20°C; $V_t$=10 ml; mechanical stirring
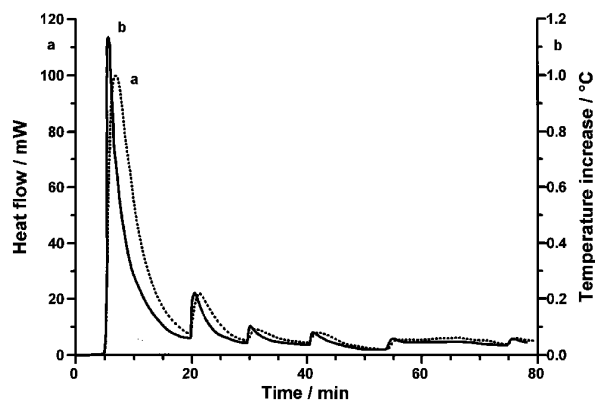
**Fig 4** Simultaneous recording of the rate of heat production and the temperature change in a gallic acid system; Initial concentrations: [GA]=0.018 M; [KBrO$_3$]=0.05 M; [H$_2$SO$_4$]=1.0 M; $t$=20°C; $V_t$=5 ml; stirred by a nitrogen gas flow; a) Rate of heat production; b) Temperature change

of oscillations, and the higher was the number of oscillations. These observations are again in accordance with the findings of Dutt and Menzinger [21].

*The HME–bromate system*

Many para-substituted phenols (PSP) in their reactions with acidic bromate exhibit temporal chemical oscillations. Our earlier investigations on these UBOs clari-
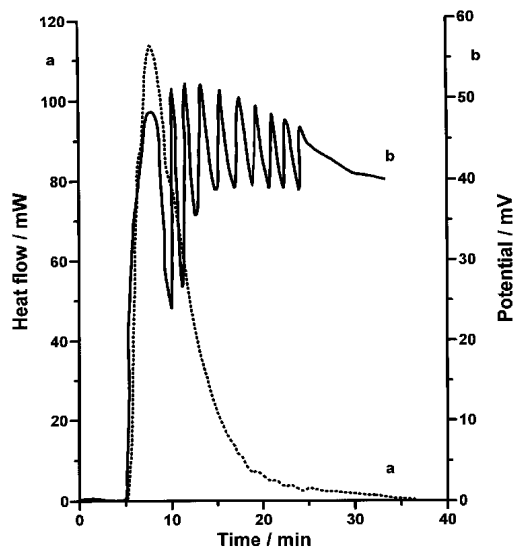


**Fig. 5** Simultaneous recording of the rate of heat production and the redox potential in a HME system; Initial concentrations: [HME]=0.018 M; [KBrO$_3$]=0.05 M; [H$_2$SO$_4$]=1.0 M; $t$=20°C; $V_t$=5 ml; stirred by a nitrogen gas flow; a) Rate of heat production; b) Potentiometric trace

fied what products have formed, and we could suggest a chemical mechanism that simulated rather well the observed temporal course of the process [16].

UBOs containing such type of an organic substrate have not been studied calorimetrically. This fact prompted us to perform calorimetric investigations on that PSP–bromate system about which mechanistic data are already available. The organic compound we selected was a phenol substituted with an N-alkyl-amine group, the HME.

With this system the calorimetric experiments were run both under isothermal and under quasi-adiabatic conditions and in many cases also simultaneous potentiometric recordings were taken.
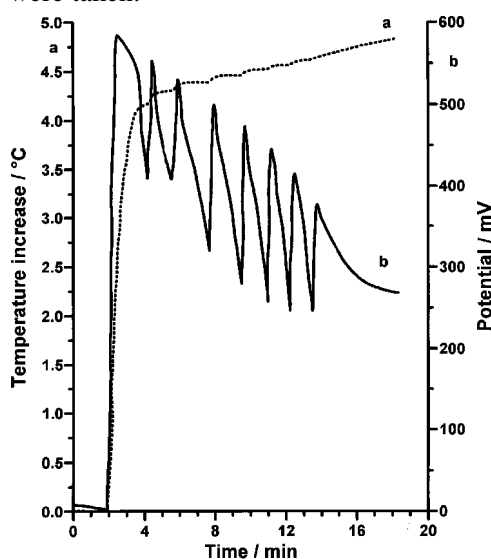


**Fig. 6** Simultaneous recording of the potential and the temperature changes under quasi-adiabatic conditions in a HME system; Initial concentrations: [HME]=0.018 M; [KBrO$_3$]=0.05 M; [H$_2$SO$_4$]=1.0 M; room temperature; $V_t$=30 ml; magnetic stirring; a) Calorimetric trace; b) Potentiometric trace

Figure 5 shows a typical isothermal run, and Fig. 6 the simultaneous recording of the potential and the temperature changes. Similar to that observed with the GA–bromate system here again during the preoscillatory period the heat output was high. In the oscillatory phase of the reaction the rate of heat production was low, considerably lower than with GA as an organic substrate.

Results obtained at various concentration ratios are compiled in Table 2.

Some runs were done at different nitrogen flow rates. The parameters of oscillation practically did not change when the flow rate was varied.

*The CHD–bromate system*

We performed calorimetric measurements both under isothermal and quasi-adiabatic conditions also on an UBO system with CHD as an organic substrate.

**Table 2** Results of isoperibolic and quasi-adiabatic calorimetry on the oscillating HME–bromate system. Abbreviations as in Table 1

| [HME]/ M | [KBrO$_3$]/ M | T/ $^oC$ | Total volume/ ml | Preper./ min | Per. time 1–2/ min | Osc. number |
|---|---|---|---|---|---|---|
| 0.018 | 0.05 | 20 | 10 | 6 | 3 | 5 |
| 0.01 | 0.05 | 20 | 10 | 3.3 | 3.6 | 3 |
| 0.018 | 0.025 | 20 | 10 | | does not oscillate | |
| 0.018 | 0.037 | 20 | 10 | 6 | 2 | 12 |
| 0.018 | 0.05 | room temp. | 30 | 1.4 | 1.4 | 6–7 |
| 0.013 | 0.05 | room temp. | 30 | 1.6 | 2 | 4 |
| 0.01 | 0.05 | room temp. | 30 | 1.6 | 2.6 | 3 |
| 0.018 | 0.033 | room temp. | 30 | 2.6 | 0.7 | 13–14 |
| 0.018 | 0.025 | room temp. | 30 | 7 | 0.8 | 17–19 |

Other conditions: [H$_2$SO$_4$]=1.0 M

In the quasi-adiabatic experiments also the potential oscillations were recorded. The preoscillatory period of the reaction was considerably longer than with the other two systems discussed above. However, the essential difference between this and the other UBOs was the absence of the sudden very high heat output (respectively temperature jump) in the very early phase of the reaction. Instead, the temperature rose slowly during the preoscillatory period and after the onset of oscillations temperature of the reaction mixture increased stepwise. (The temperature change in a single step, however, was considerably smaller than with the GA and HME systems.) This
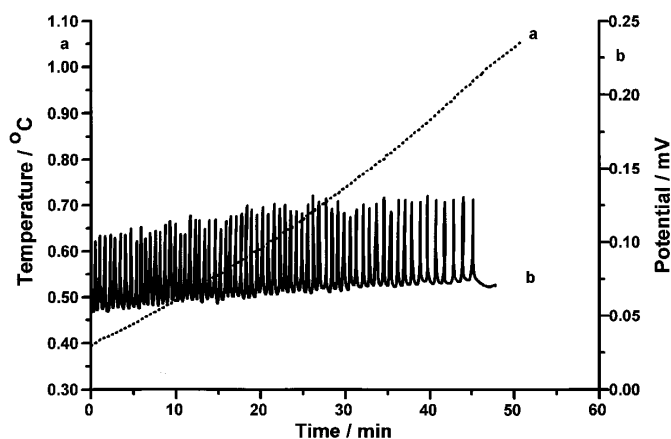


**Fig. 7** Simultaneous recording of temperature and potential change in a CHD system under quasi-adiabatic conditions; Initial concentrations: [CHD]=0.01 M; [KBrO$_3$]=0.05 M; [H$_2$SO$_4$]=1.0 M; room temperature; $V_t$=30 ml; magnetic stirring; a) Calorimetric trace; b) Potentiometric trace

value continuously increased parallel with the progress of the reaction (Fig. 7). Early during the oscillatory phase of the reaction the temperature rise in a single step was about 0.01°C and at the end of the oscillatory period about 0.046°C. In Table 3 we compiled some parameters of the oscillatory system measured under different experimental conditions.

**Table 3** Results of isoperibolic and quasi-adiabatic calorimetry on the oscillating CHD–bromate system. Abbreviations as in Table 1

| [CHD]/ M | [KBrO$_3$]/ M | $T$/°C | Total volume/ ml | Preper./ min | Per. time 1–2/ min | Osc. number |
|---|---|---|---|---|---|---|
| 0.1 | 0.025 | 20 | 10 | 84 | 1.1 | 96 |
| 0.1 | 0.025 | room temp. | 30 | 35 | 0.65 | 70–75 |
| 0.1 | 0.033 | room temp. | 30 | 34 | 0.5 | 97 |
| 0.1* | 0.025 | room temp. | 30 | 22 | 0.25 | 132 |

Other conditions: [H$_2$SO$_4$]=1.0 M; Stirring rate=500 min$^{-1}$
* [H$_2$SO$_4$]=1.5 M

Runs performed under isothermal conditions demonstrated a slow increase in heat production rate after the start of the reaction, and after a certain period of time a plateau value was reached. Then during the oscillatory phase of the reaction the heat production rate exhibited a slow increase and the amplitude of oscillations became more and more expressed (Fig. 8). This tendency can be seen more pronounced on a recording taken at a higher sensitivity (Fig. 9). After the termination of oscillations the reaction between CHD and bromate still continued, however, in a
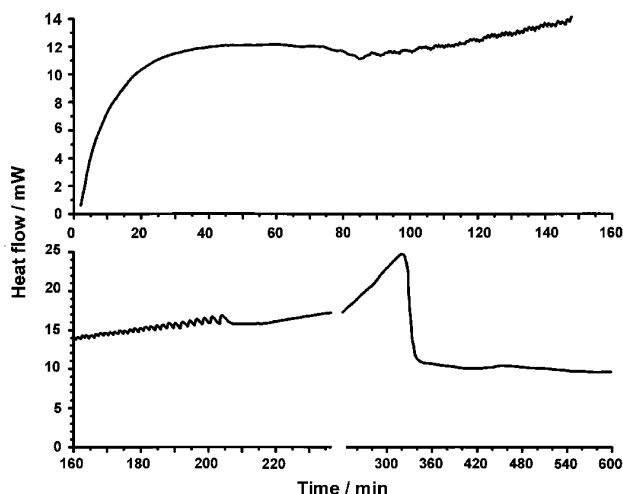


**Fig. 8** Rate of heat production measured under isoperibolic conditions in a CHD system. Please notice the change in time scale in the lower trace. Initial concentrations: [CHD]=0.1 M; [KBrO$_3$]=0.025 M; [H$_2$SO$_4$]=1.0 M; $t$=20°C; $V_t$=10 ml; mechanical stirring
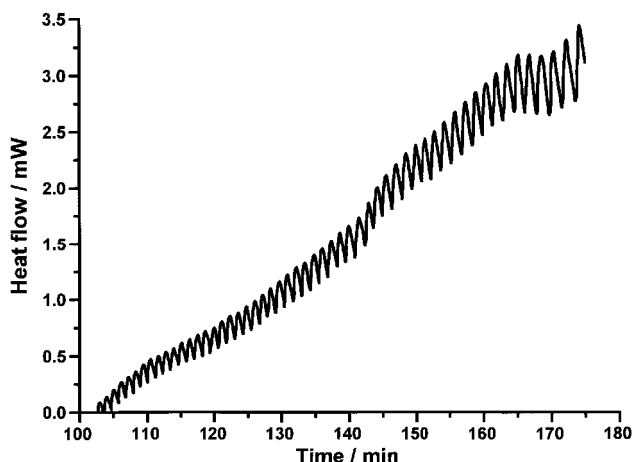
**Fig. 9** A part of the recording in Fig. 8 taken at a higher sensitivity

non-oscillatory manner and after a prolonged time the system returned to the baseline, i. e. the chemical reaction terminated.

We have to emphasize that experiments performed both under quasi-adiabatic and isothermal conditions have shown an increase in the temperature change in a single oscillatory step as the reaction progressed, unlike to other uncatalyzed systems.

## Discussion

### The GA–bromate system

The reaction between gallic acid and bromate in sulfuric acid solution is a rather involved one. Jwo and Chang [2] studied the reaction in some details and by using sophisticated analytical techniques (HPLC, NMR, GC-MS) attempted to identify the products of the reaction. They claimed that *o*- and *p*-quinone-type compounds, their bromoderivatives and also condensation products were present in the reaction mixture. The formation of the latters, however, actually lacked any analytical support. They suggested a somewhat modified reaction mechanism in which an important reaction product was an *o*-quinone that formed by the direct attack of bromate ion on gallic acid:
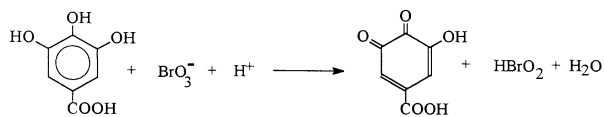


They assumed that also $HBrO_2$ and $HBrO$ can oxidize gallic acid accordingly. Parallel with the oxidation proceeded the bromination of gallic acid and its oxidation product.

Mukherjee *et al.* performed calorimetric studies on the oscillatory reaction between gallic acid and bromate ion both in the absence and in the presence of ferroine

as a catalyst [14]. They claimed that the large exothermicity at the initial phase of the reaction was followed by a short endothermic period just before the onset of oscillations, and that the latter thermal behaviour of a chemical oscillator (i.e. endothermicity) had not been reported previously. Authors, however, did not assign the endothermicity to any particular chemical reaction and even their results did not seem to support their statement. None of the processes (or elementary reaction steps) have positive enthalpy, since all the reactions occurring between bromate and an organic substrate (i.e. oxidation, bromination, oxidative bromination) and also the redox reactions between the inorganic species are exothermic ones. We assume that they misinterpreted some of the experimental results.

Calorimetric and earlier potentiometric data indicate that already in the early phase of the gallic acid–bromate reaction the chemical transformation is of great degree, and quinones and brominated derivatives of gallic acid are the main products. Investigations performed on other UBO systems containing a phenol-type organic substrate allow us to conclude that the original organic substrate is completely converted to oxidation and bromination products when the oscillatory phase of the reaction starts [15].

We found that the important parameters of the reaction were considerably influenced by the stirring rate. An increase in the stirring rate resulted in an increase of the length of the preoscillatory period as well as in the period time of oscillations. This can be explained by considering that the higher is the stirring rate the longer the system remains in the oxidized state (i.e. in that kinetic state where the bromide ion concentration is low). For, bromine which is one of the intermediates of the reaction is transferred from the reaction mixture to the atmosphere faster by the gas–air interchange at higher stirring rates. Thus less bromine remains in the solution for bromination and therefore less bromide ions are formed. According to the FKN mechanism [22] the reacting system switches from the oxidized state (where bromide ion concentration is very low) to the reduced one at a threshold bromide ion concentration. As this concentation value is reached in a longer period of time, the period time increases accordingly.

The same explanation is valid when the magnetic stirring is replaced by bubbling nitrogen gas through the solution. For, nitrogen very effectively expels bromine from the reaction mixture.

*The HME–bromate system*

Para-substituted phenols are very suitable substrates for UBOs since the variety of reactions is somewhat limited owing to the occupied para position. Naturally this is true only when the substituent is practically unreactive towards bromate. N-alkyl amine derivatives of phenol proved to be the best substrates. These organic compounds are readily soluble in water and in dilute mineral acids.

In previous years the HME-containing oscillatory system was in focus of our interest. Detailed kinetic measurements and reaction mechanistic studies revealed that the main products of the reaction with bromate are 1,2-benzo-quinone and monoand dibromophenol derivatives.
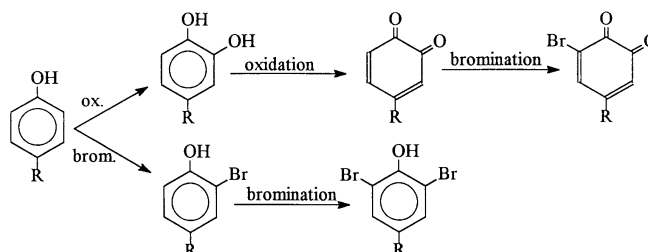
It has also been found that chemical oscillations start only when the monobromo derivatives reach a critical concentration [16].

Our calorimetric measurements show that immediately after the initiation of the reaction the rate of heat production is very high, and due to the bromate excess, after a short period of time (1–2 min) the original organic compound disappears from the reaction mixture. [This corresponds to results we have found with many UBOs (e.g., phenol, pyrogallol, gallic acid)]. However, the amount of this organic consumed in a single step in the oscillatory phase of the reaction is much less than in case of gallic acid.

Another difference between the two systems is that the nitrogen gas flow has no influence in the HME system on the above-mentioned parameters. This can be explained in terms of a difference in rates of bromination. For, HME is brominated much faster than gallic acid and therefore bromine practically does not appear in the reaction mixture, since it is immediately consumed in the bromination reaction.

*The CHD–bromate system*

Earlier experiments have shown that CHD – as an alicyclic compound – behaves differently in its reaction with bromate compared with aromatic substrates. Detailed analytical studies have disclosed that the multistep transformation of CHD into its products starts with the slow oxidation of CHD in which it is converted to 1,4-dihydroxybenzene (hydroquinone) in an aromatization reaction. Then hydroquinone is rapidly oxidized to 1,4-benzo-quinone. Synchronously with the oxidation bromination reactions proceed and bromo-CHD, bromo-hydroquinone and bromo-benzoquinone are formed [18, 23].
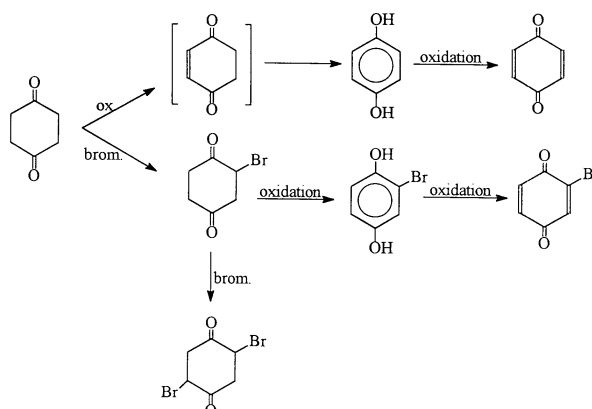
Another characteristics of the reaction is that unlike the dynamic behaviour of other UBOs in batch configuration the number of oscillations is very high. Under optimal concentration conditions even above 300.

Our calorimetric results seem to support the above described chemistry of the CHD–bromate reacting system.With this system a high and abrupt heat production in the preoscillatory period has not been observed; instead a prolonged heat production (respectively, temperature rise) had been recorded.

A temporal increase in the amount of reactants consumed in a single oscillatory step can be accounted for by considering that during the progress of the reaction an increasing amount of bromoderivatives form. They are the sources of bromide ions that play a key role in the control of bromate oscillators [24]. From analytical measurements we could calculate that in the oscillatory phase of the reaction the amount of bromate consumed in a single step was in the order of $10^{-5} M$ [25].

Our observation that in the oscillatory phase of the reaction and also in the postoscillatory period the overall heat production exhibits an increasing tendency prompts us to assume that the reaction between CHD and bromate proceeds simultaneously in oscillatory and non-oscillatory manner. With other words it is likely that chemical oscillations appear superimposed on the slowly proceeding non-oscillatory redox reaction. Only calorimetric studies could direct our attention to this rather uncommon phenomenon. Although it is true that calorimetry can not reveal the details of chemical processes, our above-mentioned observation, however, emphasizes that unexpected novel information can be gained also from calorimetric investigations.

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