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MICROCALORIMETRIC INVESTIGATIONS OF CHEMICAL OSCILLATIONS: THE ZHABOTINSKI REACTION*

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ABSTRACT

Calorimetric experiments on the autocatalytic oscillating bromination of carboxylic acids in the presence of cerium or manganese (Belousev–Zhabotinski reaction) are reported. They exhibit a strong modulation of the exothermic heat production which returns to zero under appropriate conditions and demonstrate two antagonistic effects of different time constants and heats. Under the chosen conditions the brominating agent is the limiting factor for the total reaction. By stirring the solution, the form of the oscillations can be changed or even cancelled out. As the time constant of the calorimeters is nearly the same as the period of the oscillations, it is necessary to perform a mathematical folding of the obtained thermograms to correct for the thermal inertia or to run the experiments at low temperatures.

1. INTRODUCTION

One of the most interesting results of the thermodynamics of non-equilibrium is the appearance of oscillations around a temporary steady state which corresponds to a limit cycle behaviour of the system. Many such oscillations have been found in recent years ranging from pure chemical reactions to very complex biochemical pathways in living organisms[1–3]. Moreover, together with rhythmic changes in one or more parameters of the system, temporal–spatial and pure spatial structures have also been observed[3–6].

One of the intensively studied reactions, the bromination of carboxylic acids such as malic, malonic or maleic acid in the presence of catalysts like cerium or manganese with rhythmic changes in the oxidation status of the catalyst, was first described by Belousev[7] and later by Zhabotinski and coworkers[4, 8, 9]. Since then many scientists have studied this reaction[10–20]. Nevertheless, many questions concerning the exact mechanism of these oscillations remained open.

The course of the Belousev–Zhabotinski reaction may be followed photo-

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metrically, polarographically, manometrically and calorimetrically, but only two calorimetric investigations have been conducted[14, 15]. The instrument was a quasi-adiabatic calorimeter monitoring the increase in temperature of the system. As an isothermal calorimeter of the heat flow type is more appropriate for chemical experiments, we looked for the heat per single pulse and for the total heat output during the whole period of oscillations. This paper reports the results.

2. THE CHEMISTRY OF THE BELOUSEV–ZHABOTINSKI REACTION

At present, the chemistry of the Belousev–Zhabotinski reaction is not completely clear, but the main steps have been elucidated, among others, by Zhabotinski[4, 8, 9], Kōrōs et al.[13–15], Field et al.[5, 12], Degn[10, 11] and Bornmann et al.[16–18]. For the exact description the reader is referred to the literature.

The reaction consists of the oxidation of the catalyst by bromate and a subsequent reduction by carboxylic acid. During the oxidation a monobromocarboxylic acid is formed, which is further brominated to a dibromocarboxylic acid. This acid is a strong inhibitor of the autocatalytic oxidation of the catalyst by the bromate from which the bromine is formed. The reduction of the oxidized catalyst is not influenced, so that the reduced form accumulates. As the dibromine compound is not stable and decomposes, the inhibiting properties diminish. Below a critical concentration the oxidation of the catalyst is switched on again, thus leading to oscillations in the ratio of reduced and oxidized catalyst. The oxidized form absorbs light in the visible range, so that the oscillations may be followed by changes of colour in the solution. It was found that the appearance of the oscillations is practically independent of the kind of catalyst (cerium, manganese, ferroin) and that the reaction is driven by all carboxylic acids of the type $R–CO–CH_2–COOH$.

In the case of the thoroughly studied reaction with malonic acid, the compound is transformed to monobromomalonic acid and to dibromomalonic acid. This instable inhibitor decomposes to dibromoacetic acid and carbon dioxide. The carbon dioxide may be monitored by means of manometric techniques[18] and exhibits its existence in the form of bubbles on the walls of unstirred reactions vessels. Monobromomalonic acid, dibromomalonic acid and dibromoacetic acid could be found chromatographically[16, 17]. Some authors claim that formic acid is an end product and that the free energy of this reaction drives the oscillations[12]. But no formic acid could be detected, so that other lines of decomposition must be followed.

3. METHOD AND MATERIAL

Chemical substances

(a) Potassium bromate, $KBrO_3$, 0.1 and 0.2 M.

(b) Malonic acid, $C_3H_4O_4$, 0.4 and 0.8 M; Malic acid, $C_4H_4O_5$, 0.4 and 0.8 M; Maleic acid, $C_4H_4O_4$, 0.4 and 0.8 M; (a) and (b) dissolved in 0.5 M sulfuric acid, H_2SO_4.

(c) Ceric nitrate, $Ce(NO_3)_3 \cdot 6H_2O$, 1 mM; Manganese sulfate, $MnSO_4 \cdot 1H_2O$, 46 mM; Ferroin, 4 mM; all in bidistilled water. In each experiment a total amount of 6 ml of (a) and (b) plus constant 0.4 ml of (c) was used. Thus, the amount of (a) and (b) ranged from 0.5 to 5.5 ml.

Microcalorimeters

Two types of calorimeter were used, both equipped with a mechanical stirring device[21] and a glass reservoir just above the calorimetric vessel which contained 0.4 ml of the catalyst. After adjustment of the thermal equilibrium the tempered catalyst could be added from the outside by means of a syringe, starting the reaction.

The first calorimeter was a Calvet-microcalorimeter (Setaram/Lyon) with an effective volume of 15 ml and a sensitivity of 61 $\mu V\ mW^{-1}$, the second was a MCB calorimeter (Arion/Grenoble) with a volume of 15 ml and a sensitivity of 43 $\mu V\ mW^{-1}$. The Calvet instrument always worked at 30 °C, while the MCB was sometimes placed in a cold room to obtain reaction temperatures of 10 °C.

Other equipment

The optical experiments were performed with a spectral photometer Beckman DB-G and an appropriate recorder at room temperature. A few experiments on the production of carbon dioxide were run with a Warburg apparatus (Braun/Melsungen).

4. RESULTS

General findings

In most of our experiments a system of potassium bromate, malic acid and manganese sulfate was used. Malonic acid, which is most often cited in the literature, is nearly equally suitable, whereas with maleic acid a crystalline precipitate appears after a short period, which stops the oscillations.

Figure 1 represents a thermogram of a stirred system of malic acid. Immediately after addition of the catalyst the heat production starts. In contrast to findings in the

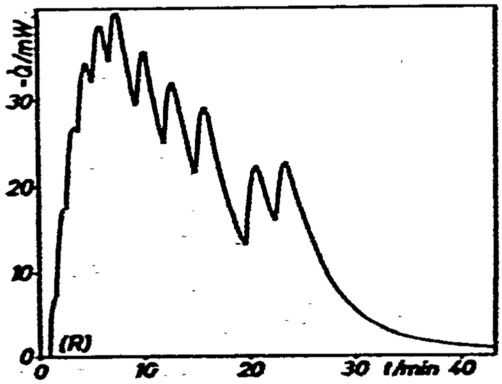

Fig. 1. Thermogram—heat flow versus time—of a stirred solution of maleic acid at 30 °C.

literature, there is no induction period for the oscillations. Because of the thermal inertia we do not observe distinct pulses in the first phase but a somewhat smoothed curve. Later on the single pulses become clearer. Amazingly, under these conditions of stirring and at a temperature of 30 °C, there is a sudden break and a return to the experimental zero line. The slope of this decline follows the cooling law with a time constant equal to that of the calorimeter. That means that the main heat producing effect is switched off instantaneously without appearance of a further exothermic reaction.

There are minor as yet unknown parameters which may change the form of the thermograms significantly. Under slightly varied conditions at 30 °C and nearly always at 10 °C the oscillations stay until the very end of the reaction (Figs. 2 and 3). In this case they approach the zero line, indicating that there is a phase of approxi-

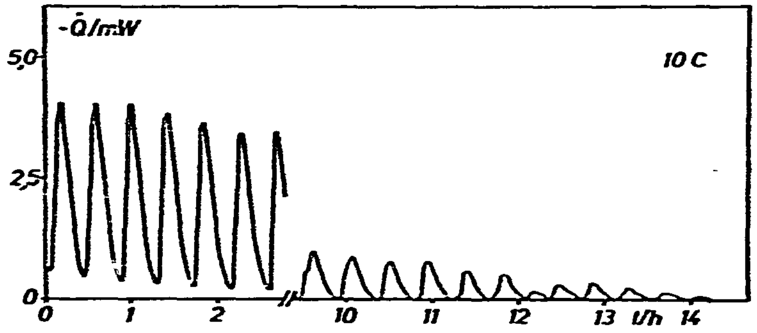

Fig. 2. Thermogram of an unstirred solution of maleic acid at 10 °C.

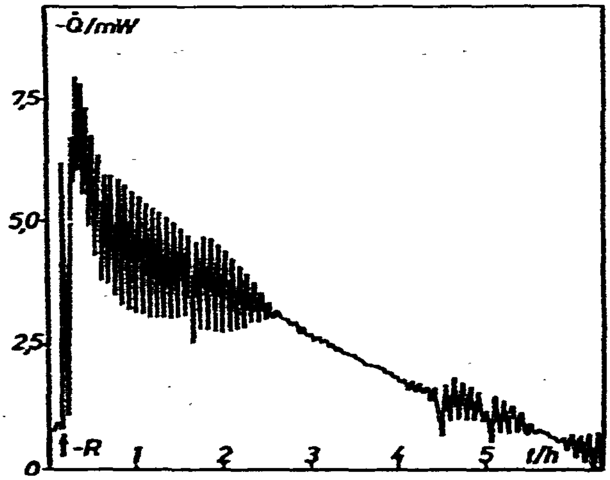

Fig. 3. Thermogram of an unstirred solution of maleic acid at 10 °C with modulated oscillations.

mately no heat production. In the line of experiments, there may be different types of oscillations. Very often the large pulses show small structures in themselves which stay for a large number of oscillations. On the other hand, the oscillations may be modulated with a frequency which is 5 to 20 times smaller than the original. Figure 3 shows a thermogram at 10°C with several packets of oscillations. This structure probably points to a second, less active inhibiting effect in the reaction, perhaps from the dibromoacetic acid[11]. These modulations sometimes also appear in the photometric records, but always in the thermograms at low temperatures.

Field et al.[12] demonstrated that the oxidation of the catalyst is a very quick second-order reaction. The reduction of the catalyst by the monobromocarboxylic acid is some orders of magnitude slower, so that it may be followed photometrically. As the reduction is accompanied only by minor heat production, it is normally not detected in the calorimeter, so that the falling slope exhibits the time constant of the instrument. Therefore, it is correct to calculate the heat production of the system as single heat bursts[19].

With the concentration of $KBrO_3$ used, the number of oscillations may be greater than 200 with a maximum duration of the oscillation period of 6 h at room temperature and of several days at 10°C. Number and duration depend nearly on the square of the $KBrO_3$ concentration, as does the total heat output. The frequency is highest at the beginning of an experiment and is sometimes halved by the end. Therefore, it is necessary to state the time in the experiment for which the frequency is given. Detailed information will be published elsewhere.

Heat measurements

The maximum heat production or maximum heat flow as taken from the largest deflection in the thermogram increases linearly with the $KBrO_3$ concentration (Fig. 4). The total heat production during the experiment is determined as the area between the heat flow curve and the zero line. This heat plotted as a function of the initial

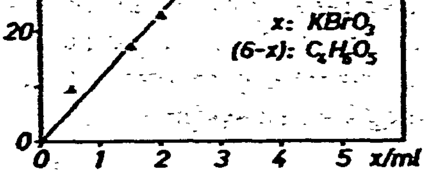

Fig. 4. Maximum heat flow $\dot{Q}'$ as function of the amount of bromate (0.1 M) in a stirred maleic acid solution.

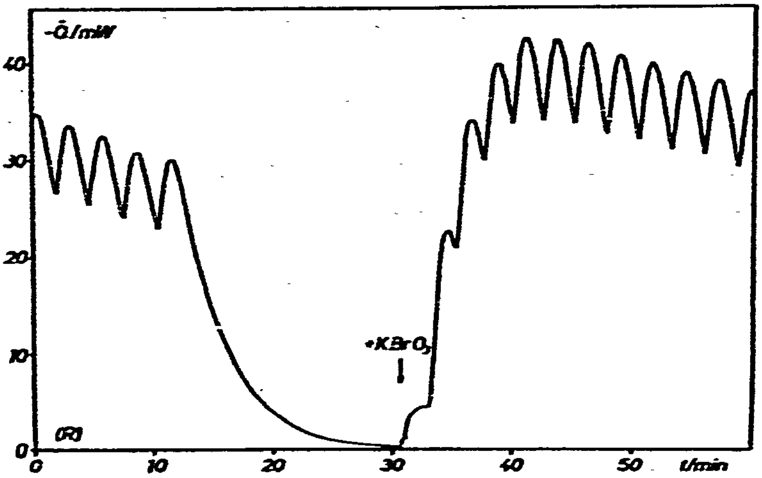

Fig. 5. Thermogram of a stirred solution of maleic acid. At the indicated point (↓) 1 ml of bromate (0.1 M) was added.

$KBrO_3$ concentration yields a parabolic slope with a power of 1.93 for stirred solutions and 1.85 for unstirred ones, which are identical within the limits of error. $KBrO_3$ is thus the limiting factor in the reaction, even at very low concentrations. This is clearly demonstrated by the fact that after the addition of more $KBrO_3$ to a solution in which the oscillations have died out, the oscillations recur (Fig. 5).

If one assumes the bromination of the malonic acid to monobromomalonic acid, dibromoacetic acid and carbon dioxide[16–18], one may calculate an enthalpy change of −470 kJ per mole $KBrO_3$. In our experiments the heat is somewhat smaller. This indicates that the bromate is not totally consumed, although it is the limiting factor. This is in agreement with the finding that oscillations are only possible in a limited concentration range of the reactants. The heat produced per oscillation ranges from 3 to 6 J, independent of the initial bromate concentration. In experiments with a sudden break in the oscillations (Figs. 1 and 5) the heat per pulse increases with time, whereas in the case of dying oscillations they vanish towards zero. This is the behaviour described by Körös et al.[14, 15]. In their quasi-adiabatic system the temperature jumps decrease with time. Calculated per milliliter the corresponding enthalpies are larger by a factor of appr. 1.5 than those found in our experiments. But as the frequencies also differ for the two types of experiments, these results are not contradictory. At room temperature the frequency of the oscillations is too high to be correctly resolved by the calorimeter, because the time constant of the instrument is comparable with the period of the oscillations. Taking into account the thermal inertia of the system, the "true" heat production curve was calculated from a normal thermogram. Under these conditions, the heat production returns to zero between two pulses, i.e., there is no long-lasting exothermic process in the system.

Influence of temperature

The same results are obtained by lowering the reaction temperature to 10°C.

Following the Q_{10} rule, the period length should increase by a factor larger than 4 so that the instrumental time constant becomes small compared with this period. Under these conditions, the heat bursts return to zero, as expected (Fig. 2). They never cross the final experimental zero line, demonstrating that there may be oscillations up to, but not around the equilibrium[11].

The Arrhenius plot of the frequencies at various temperatures versus the reciprocals of the temperatures yields a straight line between 10 and 50 °C. The slope equals an activation enthalpy of 60 kJ mol^{-1}, while Kōrōs[19] reports 67 kJ mol^{-1} for different catalysts of this reaction.

Additional results

In the Belousev–Zhabotinski reaction, periodic spatial inhomogeneities are well known[4, 6]. After a short induction period, wandering coloured bands may

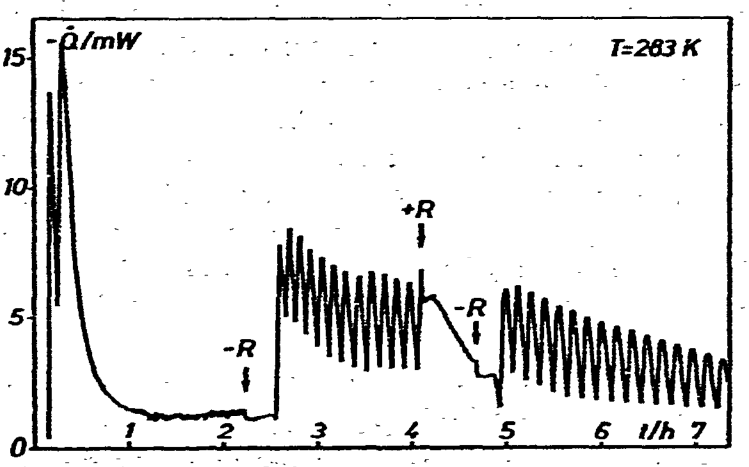

Fig. 6. Influence of stirring (+R) and not stirring (−R) on the appearance of oscillations in a system of maleic acid at 10 °C.

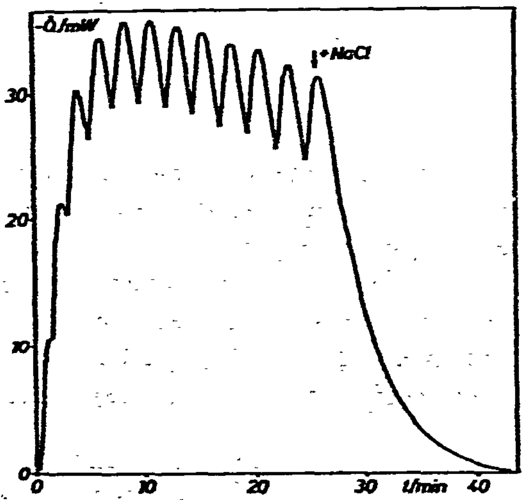

Fig. 7. Poisoning of the Belousev-Zhabotinski reaction by the addition of small amounts of sodium chloride (↓ NaCl).

travel along the reaction vessel. As the appearance is due to the oxidation of the catalyst and combined with the heat bursts, there should be heat bursts all over the vessel with phase differences. The total heat production monitored by the momentary heat flow as the sum of all heat processes should therefore be a smoothed curve.

To obtain a complete homogeneity of the system and in this way a synchronization of the oscillations, the contents of the vessel were stirred. At room temperature the oscillation becomes more pronounced than in the unstirred solution. If the stirrer is switched off during the oscillation the amplitude drops by a factor of appr. 2 without significant influence on the frequency. On the other hand, by stirring an initially unstirred solution, the amplitudes may increase six- fold with a small shift in the phase. The heat production may cease at a very high level (Figs. 1 and 5) only in stirred reactions, while in unstirred reactions the oscillations die out (Fig. 2). At low temperatures, stirring may disturb the oscillations completely, as shown in Fig. 6, leading only to an unstructured exothermic reaction. This effect has not been explained yet.

Traces of chloride ions may totally inhibit oscillations in the Belousev–Zhabotinski reaction[8, 12]. If NaCl is added to an oscillating solution in the period of decolouration, i.e., the reduction of the catalyst by carboxylic acid, the reduction proceeds to the end without a new pulse and the heat production falls to zero. If NaCl is added during the first part of an oscillation the complete pulse is performed with the subsequent return to zero (Fig. 7). This indicates that the chloride ions poison the autocatalytic oxidation of the catalyst and block the feed-back system. However, this reaction is so quick that no direct influence can be seen within one oxidation period (Fig. 7).

All calorimetric experiments were run with a total volume of 6 milliliters. The composition was varied from 0.5 ml $KBrO_3$ + 5.5 ml malic acid to 5.5 ml $KBrO_3$ + 0.5 ml malic acid in steps of 0.5 ml. With 0.5 ml $KBrO_3$ no oscillations could be detected, whereas with 5.5 ml there was a long induction period followed by small oscillations. Between 1.0 and 5.0 ml $KBrO_3$ the oscillations start immediately in the same form.

DISCUSSION

The oscillations in heat production accompanying the different states of oxidation and reduction in the Belousev–Zhabotinski reaction clearly demonstrate that in a closed—but not isolated—calorimetric system oscillatory kinetics are applicable. In adiabatic systems oscillations occur, too[14, 15]. Moreover, as the temperature rises in the heat conduction calorimeter are very small because of the good conductivity of the heat-flow meter (in the order of 10^{-3} K), the examined reaction does not belong to the class of thermokinetic oscillations where the feed-back loop is driven by the heat of reaction.

It was postulated that in closed homogeneous systems, oscillations should be impossible[22]. This general statement must be wrong, as the principle of detailed balancing is not applicable far from equilibrium[11]. Our experiments prove that oscillations are possible in unstirred—i.e., perhaps inhomogeneous—as well as in homogeneous reactions. The transition from unstirred to stirred solutions at lower temperatures with a cease of the oscillation in heat production shows the influence of partial or total homogeneity for the oscillating reaction. It may be that at higher temperatures, and therefore higher reaction rates, a partial inhomogeneity remains in the system in spite of the stirring.

Many authors claim that there must be an induction phase before the oscillations start. Under the chosen experimental conditions, the reaction starts immediately after addition of the catalyst (Figs. 1 and 7). The first oscillations are hard to resolve fully in the thermogram because of the thermal inertia of the system. But at lower temperatures they are quite distinct (Figs. 2 and 3). Still unexplained are small or even undetectable changes in the outer parameters which make the oscillations stop or alter the rhythm of the reaction (Fig. 1, later part). Perhaps, they are due to incomplete homogeneities during stirring, to the formation of carbon dioxide bubbles or to poisoning effects like that with sodium chloride (Fig. 7). But as the system is very complex, other components may also be of influence. Two forms of oscillations in relation to the equilibrium are imaginable: (a) oscillations around the equilibrium during the approach to it, and (b) oscillations around quasi-steady states during this approach[11]. (a) is excluded by the principle of detailed balancing, while the reported experiments demonstrate situation (b). The amplitudes of the oscillations decrease with decreasing distance to equilibrium and finally die out (Fig. 2), but they never cross the experimental zero line between exothermic and endothermic reactions.

All calorimetric and spectrophotometric experiments clearly demonstrate that in the studied closed system, the oscillations vanish with time, because they are only possible in a special range of concentrations of the different reactants. If the reacting volume is connected to a container of fresh solution, the oscillations can be kept alive infinitely. Knowing the heat of reaction and measuring the heat evolved until the break in the oscillations of the thermogram, one can roughly calculate the boundary conditions. They correspond to those found for initial concentrations of reactants which allow or exclude oscillations. A repeated addition of bromate after the end of the reaction with a recurrence of the oscillations underline these results.

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