

CALORIMETRIC STUDY OF THE COMPONENT STEPS OF OSCILLATING CHEMICAL REACTIONS

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Abstract

The complexity of oscillating chemical reactions makes difficult a direct calorimetric study of them. It is more advantageous to carry out studies of the component steps and then try to put the parts together. Here, a mass-flow heat conduction calorimeter was used to study component reactions of two of the principal chemical oscillators. The studied reactions were: the net reaction of the inorganic set of the Belousov–Zhabotinsky reaction ($\text{BrO}_3^- + 4\text{Ce}^{3+} + 5\text{H}^+ \rightleftharpoons 4\text{Ce}^{4+} + \text{HOBr} + 2\text{H}_2\text{O}$), and the Dushman reaction ($\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$), which is a component of the Bray–Liebhafsky oscillator. The experimental values of the enthalpies of these two reactions are reported in this work.

Keywords: Dushman reaction, inorganic set of the BZ reaction, mass flow heat conduction calorimeter, reaction enthalpies

Introduction

The study of oscillating chemical reactions has been based mainly on kinetic aspects [1]. There have also been some studies on the thermochemistry of this type of reactions [2, 3], however the number of publications on this topic is by far, less than those on kinetic topics [4].

Oscillating chemical reactions are puzzling and their mechanisms are complex and have been deeply studied, but there are still several aspects to be understood. One of the not very well explored areas is the heat of the reactions. Because of the complexity of the systems, a study of the reaction heat of the chemical oscillator would be very difficult and only little information would be obtained. Then, it is better to start this kind of research with parts of the total oscillator.

The reaction: $\text{BrO}_3^- + 4\text{Ce}^{3+} + 5\text{H}^+ \rightleftharpoons 4\text{Ce}^{4+} + \text{HOBr} + 2\text{H}_2\text{O}$, which is the net reaction of the inorganic set of the Belousov–Zhabotinsky (BZ) reaction has a known mechanism [5, 6] but not an extensive calorimetric study. The heat of this reaction can be calculated from the heats of formation of the involved species, but an experimental

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study is necessary in order to confirm the calculated value. A previous publication of an experimental value does not clearly state how it was obtained [7].

In this work, we report an experimental determination of the reaction heat of the inorganic set of the BZ reaction. We also report the reaction heat of the Dushman reaction ($\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$), for which the mechanism is still matter of discussion in the literature [8–11].

Experimental

Isothermal mass-flow heat conduction calorimeter

The calorimeter used consists of the following parts:

The calorimetric cell is a cylindrical glass vessel of 33 cm³ internal volume with four inlets at the bottom and one outlet at the top, equipped with a magnetic stirring bar and one resistor for the electric calibration of the apparatus.

The calorimetric sensors are four thermopiles of 127 unions each one (Melcor CP 1.0-127-05L) that are in very good thermal contact with the cell through an inner aluminum block that surrounds the calorimetric cell.

The primary deposit of heat is an outer aluminum block of 20×20×3 cm with a square hole in the middle in which the calorimetric cell, the inner block and the thermopiles, fits exactly.

The previously mentioned parts are placed in a tightly sealed metallic submarine box which is immersed in a water thermostat at 25.000±0.001°C. The total set is placed in a thermostated room at 25.0±0.2°C. Figure 1 shows a schematic representation of the calorimeter.

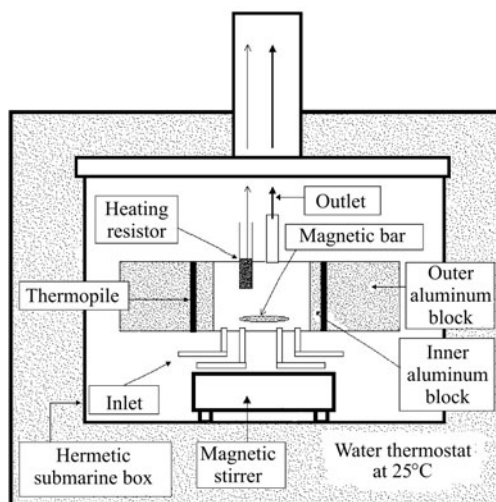


Fig. 1 Schematic diagram of the mass flow heat conduction calorimeter

Injection system: The calorimetric liquids are conducted to the reaction cell by a peristaltic pump (Master Flex 7520-25), at various flow rates, but the results show dependence with the flow; then, in the present work all experiments were carried out at only one flow, 1 mL min^{-1} .

Data acquisition and processing: The thermoelectric potential generated by the thermopiles due to the heat transfer process is acquired by a digital precision multimeter (Hewlett-Packard 3478A) with sensitivity of $0.1 \mu\text{V}$, which is connected to a personal computer by a GPIBNI-488.2 interface (National Instruments). Data acquisition and processing are performed by software developed in our laboratory by Barragán [12].

The more important characteristics of the calorimeter are shown in Table 1.

Table 1 Characteristics of the used calorimeter

Parameter	Value
1. Maximum noise (from peak to peak)	1.11 mWh^{-1}
2. Constant of the calorimeter (K_E) Inorganic subset of the BZ reaction	$11.3 \pm 0.7 \text{ WV}^{-1}$
3. Constant of the calorimeter (K_E) Dushman reaction	$12 \pm 2 \text{ WV}^{-1}$
4. Constant of the calorimeter (K_O) Chemical calibration (NaOH-HCl and THAM-HCl)	$11 \pm 1 \text{ WV}^{-1}$

Baseline

In order to obtain the baseline, water is flowed in to the vessel. After the baseline is obtained, one of the reagents corresponding to the particular experiment is flowed in; when the new steady state is reached, the second reagent is flowed in and the heat of the reaction is recorded. Finally, the electric calibration is made. Every point in this process is show in Figs 2 and 3.

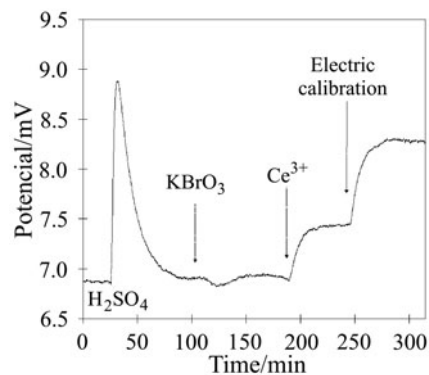


Fig. 2 Calorimetric record of the oxidation reaction of 0.046 M Ce^{3+} with 0.1 M BrO_3^- in $1 \text{ M H}_2\text{SO}_4$. BrO_3^- is introduced first to the calorimetric cell

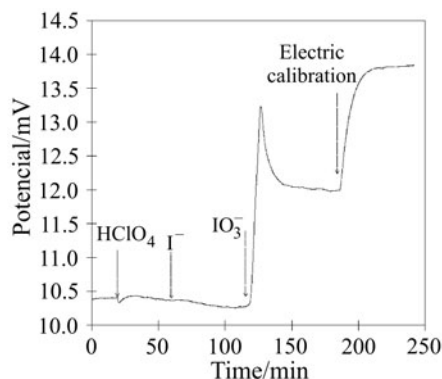


Fig. 3 Calorimetric record of the Dushman reaction, $[\text{IO}_3^-]_0=0.01\text{M}$, $[\text{I}^-]_0=0.01\text{M}$ and $[\text{HClO}_4]_0=0.15\text{M}$. I^- is introduced first to the calorimetric cell

Chemical calibration

The accuracy and precision of the calorimeter were evaluated by determining the heat of neutralization of HCl with NaOH and the heat of protonation of trihydroxymethylaminomethane (THAM) by HCl, which are traditional calorimetric standards [13–16]. HCl Fisher 36% and NaOH Merck AR were used without further purification. THAM Fisher was recrystallized four times in water.

Oxidation of Ce^{3+} with BrO_3^- in $1\text{M H}_2\text{SO}_4$

The KBrO_3 was Merck, and recrystallized from $1\text{M H}_2\text{SO}_4$ and then from water. $\text{Ce}(\text{NO}_3)_3$ was Merck, and used without additional purification. Solutions of 0.2M KBrO_3 and 0.0921M Ce^{3+} in $1\text{M H}_2\text{SO}_4$ were used and diluted $\frac{1}{2}$ on the calorimetric cell. The reactants were introduced to the calorimetric cell, in three ways: 1. Introducing first the bromate, 2. Introducing first the Cerium and 3. Simultaneous inlet of reagents.

IO_3^- with I^- in HClO_4 reaction

The KIO_3 and the KI were Merck AR. Solutions 0.2 or 0.04M KIO_3 and 0.2 or 0.04M KI were used and diluted $\frac{1}{4}$ on the calorimetric cell. The protocol of work was the same as in the previous reaction. The reported results are in all cases, the average of at least three experiments.

Results and discussion

Chemical calibration

The value reported in Table 1, $11 \pm 1 \text{ WV}^{-1}$, for the constant of the calorimeter using the chemical calibration is an average of 14 experiments, seven with the reaction NaOH-HCl and seven with the reaction THAM-HCl .

Heat of the reaction $BrO_3^- + 4Ce^{3+} + 5H^+ \rightleftharpoons 4Ce^{4+} + HOBr + 2H_2O$

The calorimetric results of our study are shown in Table 2, and Fig. 2 shows a typical experiment. Ce^{3+} is used as the limiting reagent in 0.0461M concentration. A parallel experiment was carried out to determine the percentage conversion to Ce^{4+} , because it is known that this reaction does not go to completion [17]. The concentration of Ce^{4+} was followed spectrophotometrically by the absorption at 317 nm and using a calibration curve. A conversion of 37% to Ce^{4+} was found. This aspect makes a difference with the previous work of Körös [7], who found a reaction heat of $-26.6 \text{ kJ mol}^{-1} BrO_3^-$ ($-6.65 \text{ kJ mol}^{-1} Ce^{3+}$) but did not give details of the experiments. The previously reported value is 2.9 times lower than our average result ($-77.2 \text{ kJ mol}^{-1} BrO_3^-$ or $-19.3 \text{ kJ mol}^{-1} Ce^{3+}$). The main difference in the determinations is that Körös do not take into account the percentage conversion of the reaction. Moreover, our experimental value is closer to that obtained from the calculation using the heats of formation of the species involved in the net reaction ($-70.4 \text{ kJ mol}^{-1} BrO_3^-$ or $-17.6 \text{ kJ mol}^{-1} Ce^{3+}$) [4, 18]. Additional computer simulations [4, 19] of the reaction heats of the component steps give a good agreement with our experimental results.

Table 2 Reaction heat for the oxidation of 0.046M Ce^{3+} with 0.1M BrO_3^- in 1M H_2SO_4

Injection order	K_E/WV^{-1}	$\Delta H_{R-K_E}/kJ \text{ mol}^{-1} Ce^{3+}$	$\Delta H_{R-K_Q}/kJ \text{ mol}^{-1} Ce^{3+}$
Bromate–cerium	11.9	-20.9	-19.7
Cerium–bromate	10.5	-16.4	-17.3
Simultaneous	11.6	-21.8	-19.4

K_E – electric calibration constant and K_Q – chemical calibration constant

On the other hand, it is interesting to notice that introducing first the stoichiometrically limiting reagent (Ce^{3+} in this case) a peak should appear, as shown in Fig. 3 for the Dushman reaction, but this is not the case because this reaction is slower than the Dushman reaction and the evolved heat and the heat of reaction is smaller. Only 37% of the total heat of the reaction is produced because it only goes to 37% conversion. In summary, the difference in behavior between the net reaction of the inorganic set of the BZ reaction and the Dushman reaction, can be accounted for the equilibrium of the first one and because the second one goes nearly to completion.

Heat of the Dushman reaction ($IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$)

The experimental results are listed in Table 3, and Fig. 3 shows a typical experiment. The non-homogenous precipitation of I_2 constitutes a source of irreproducibility of the results and the obtained reaction heat is greater than the calculated from the heat of formation of the involved species ($-68 \text{ kJ mol}^{-1} I^-$) [4, 18]. The reaction goes almost to completion (to check this, titrations of IO_3^- were made simultaneously with the calorimetric experiments), and then the peak is notorious in the experiments when the limiting species (I^- in this case) is introduced first to the calorimetric cell, Fig. 3.

Table 3 Heat of the Dushman reaction

Injection order	$[KI]_0=[KIO_3]_0/M$	K_E/WV^{-1}	$\Delta H_{R-K_E}/kJ\ mol^{-1}\ I^-$	$\Delta H_{R-K_Q}/kJ\ mol^{-1}\ I^-$
Iodate-iodide	0.05	10.7	-76.1	-79.0
Iodate-iodide	0.01	12.2	-120.0	-109.0
Iodide-iodate	0.01	12.5	-116.0	-98.3
Simultaneous	0.01	14.4	-89.9	-69.3

In order to avoid the precipitation problem, it is necessary to work with lower concentrations of I^- but then the heat evolved is very close to our detection limit. Therefore, this is not a convenient solution at least in this work.

Conclusions

The heat of the reaction $BrO_3^- + 4Ce^{3+} + 5H^+ \rightleftharpoons 4Ce^{4+} + HOBr + 2H_2O$ in 1M H_2SO_4 determined in this work was found to be significantly different from the previously reported value. Our experimental result shows better agreement with the one calculated from the heats of formation of the involved species.

The heat of the Dushman reaction determined is more negative than the value calculated from the heats of formation of the involved species. The precipitation of I_2 is proposed to be the source of this difference and of the lack of reproducibility of the results. However, more detailed calorimetric work is needed in order to better account for these results.

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