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Thermal behavior of Belousov-Zhabotinskii reactions with Ce(IV) salts measured by heat exchange calorimetry of flow type involving simultaneous observation of potentiometric oscillations[1]

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Abstract

Thermal and potentiometric oscillations of Belousov-Zhabotinskii reactions catalyzed by Ce(IV) salt were simultaneously observed in a continuously stirred tank reactor. A heat exchange calorimeter of flow type was assembled. An Ag-AgBr electrode and one end of salt bridge were incorporated in the sample and reference vessels. Three kinds of stock solutions in 0.200 M sulfuric acid were used in typical runs, at concentrations of 0.420 M for potassium bromate, 0.900 M for malonic acid and 3.00 mM for ammonium cerium(IV) sulfate. Each reaction solution was introduced to the sample vessel of 50.86 cm^3 via three flow paths in the range of flow rate from 0.985–21.46 $cm^3\ min^{-1}$ or of residence time τ from 3098 to 142 s. The total heat effect Q and the potential difference of bromide ions E in every oscillation were observed against time t and recorded on a Y–t recorder. Q (in Joules) was monotonously decreased with τ and each oscillation cycle T_c of Q and E showed a maximum at $\tau = 1053$ s. The high period of E which corresponded to the heat evolving period was prolonged with decrease in τ. At $\tau = 144$ s, irregular oscillations in cycle were observed. When all the components were concentrated twice, chaotic oscillations were obtained at $\tau = 1053$ s. By changing each concentration of four components to one half and twice, Q and E versus t curves were also observed.

Keywords: Heat exchange calorimetry; Belousov-Zhabotinskii reaction; Ce(IV) salts; Potentiometric oscillations

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1. Introduction

Belousov-Zhabotinskii (BZ) reactions are well known as chemical oscillation reactions in the non-equilibrated state [1]. In the presence of metal catalyst, an aqueous mixture of bromate ions in acid as an oxidant and malonic acid as an organic reductant reacts autocatalytically to construct the temporal and/or spatial structures. When the catalyst indicates a different color in the oxidized and reduced states, such as ferriin/ferroin, the color of the solution may change periodically between reddish orange and blue as temporal oscillations. If the solution is placed in a depth of 1 or 2 mm in a petri dish, mosaic patterns appear as spatial oscillations.

Many potentiometric studies in a continuously stirred tank reactor (CSTR) have been reported [2,3]. In this flow type of experiment, reaction materials necessary for a chemical oscillation may be supplied steadily, so stable oscillation should continue for a long time.

As general characteristics of a non-linear reaction, however, the oscillation behavior may largely be affected by such experimental conditions as the initial concentration of each reaction material, the rotation speed of the magnetic stirrer [4], inlet flow rate or residence time in the reaction vessel, and small temperature change of reaction circumstances. The repeatability of oscillation reactions may be poor, even if the same reaction conditions are maintained. Therefore, the simultaneous estimation of necessary information concerning chemical and physical properties may be indispensable for quantitative discussions of BZ reactions.

Reports on calorimetric studies of BZ reactions are much fewer than potentiometric and spectrometric studies, and less than 20 reports may be available. Körös and his coworkers [5] have studied them calorimetrically. Lamprecht [6] reported fundamental data by means of batch and flow microcalorimeters, for which sensitive isothermic or isoperibolic type were used. However, he had some problems. Roelofs [7] also carried out studies in the CSTR, but he did not show a thermogram. In conventional adiabatic calorimetry, instrumentation in a CSTR may not be suitable for following BZ reactions precisely at constant temperature, owing to their larger heat evolution. On the other hand, the authors developed heat exchange calorimetry of flow type [8]. Sample and reference vessels were fixed in a water bath, in which the temperature of the water was controlled at a constant level. Heat released in the sample vessel was exchanged freely with the ambient water and the thermal condition in CSTR was well maintained in order to study the calorimetric behavior of chemical oscillation reactions.

In the present study, it was considered that calorimetric data in CSTR with differences in essential reaction conditions, such as inlet flow rate, residence time and concentration of each reaction material, were necessary for discussing the relation between the heat evolving behavior and oscillation mechanism. The heat exchange calorimeter of flow type, for which all the theoretical background is omitted in this report, was assembled for measuring the thermal behavior of chemical oscillations in BZ reactions catalyzed by a Ce(IV)/(III) salt system and a potentiometric cell was also incorporated. Potentiometric oscillations of bromide ions were simultaneously followed in the same reaction vessel. The relation of inlet flow rate v_s and residence time τ in the reaction vessel to affect release Q and potential difference E in each oscillation cycle was observed against time t.

2. Experimental

2.1. Reagents

All the reagents used were of guaranteed grade and used without further purification. The chemical oscillation systems were composed of potassium bromate, malonic acid (MA), ammonium cerium(IV) sulfate (Ce(IV) salt) and sulfuric acid. Stock solutions and reactant solutions introduced to three sample inlets were prepared in 0.200 M sulfuric acid to prevent large heat of dilution of the three stock solutions. The concentrations were 0.420 M for $KBrO_3$, 0.900 M for MA and 3.00 mM for Ce(IV) salt. Potassium nitrate and agar for a salt bridge and potassium chloride for potentiometry were also of guaranteed or reagent grade and used without further purification. Deionized water was used after distillation.

2.2. Apparatus

A CSTR composed of calorimetric and potentiometric parts was assembled, for which the fundamental concept of a heat exchange calorimeter of flow type was almost the same as reported previously [8]. The vessel S shown in Fig. 1 was made of glass with a ground stopper with inlets for the three flow paths of the reactant solutions; an outlet for overflow, a thermistor, a heater element, an indicator electrode for bromide ions and one end of a salt bridge for potentiometry were fixed by taking into consideration the rotating direction of the magnetic rod in the vessel. The vessel S and a reference vessel R with the same construction and geometric configuration as S were fixed with a magnetic stirrer of submarine type (M-3, Iuchi Seieido Co., Tokyo), and then placed in the water bath for which an acryl box $30 \times 30 \times 45\ cm^3$ in size was used, filled with 36 dm^3 of water. The bath water was maintained at 25.0 ± 0.1°C by a temperature controller (CTE220, Taiyo Kogyo Co., Tokyo), and agitated heavily by a motor-driven stirrer (30 W, LT-31, Yamato Kagaku Co., Tokyo).

Heater elements for Joule heat in S and R were made of metal-wound resistors (1/8 W, 985 Ω and 999 Ω, respectively) coated with epoxy resin paste. A constant B and the resistance R of a thermistor defined as $R = A \exp(BT^{-1})$ where T is absolute temperature in K, were observed for the elements used in S and R (MB, Techno Seven Co., Yokohama). The B constants were estimated to be 3455.0 K and 3455.3 K, respectively. Their resistances were 5.605 kΩ and 5.586 kΩ, respectively, at 25.0°C. The observed temperature change of every chemical oscillations was transduced to the electric signal as the output of a Wheatstone bridge via the thermistor in each vessel. Total heat effect of every chemical oscillation Q was calculated by an on-line analog computation circuit composed of a single operational amplifier. The output voltage E_0 or the Q versus t curve was recorded on a 2-pen strip-chart recorder (R-02, Rika Denki Co., Tokyo).

The piping for flow paths in each vessel should be thin for the sake of effective heat capacity, but the flow paths of the solution were lengthened near the magnetic rod in order to mix immediately in the vessel. The mixing speed in the work was selected to be 1065 rev. min^{-1} by trial and error.

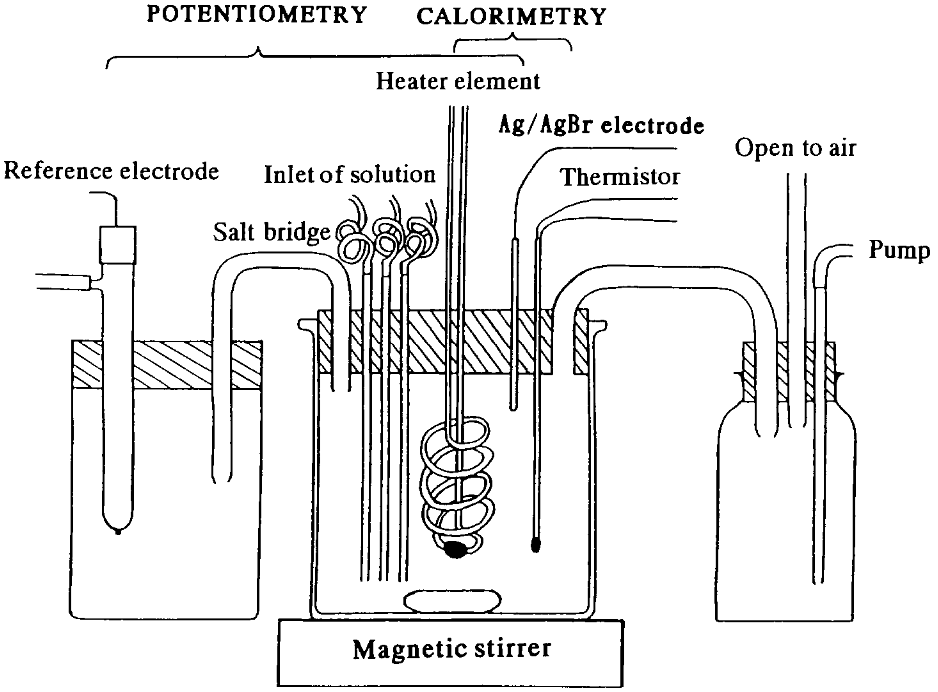

Fig. 1. Schematic sample vessel in the heat exchange calorimeter of flow type combined with a potentiometric cell.

The potentiometric part in Fig. 1 was set up as usual. It was composed of a commercially available saturated Ag-AgCl electrode (HC-205, Toa Dempa Kogyo Co., Tokyo), an agar salt bridge of potassium nitrate and the bromide indicator electrode which was made of a silver rod 2 mm in diameter as the Ag-AgBr electrode. The silver rod was also made as short as possible to minimize heat leakage and heat capacity. In the vessel R, there is no need for potentiometric measurements, but one end of the salt bridge and a silver rod were installed to compensate several calorimetric factors.

The reaction solutions were sent to S by using peristalsis pumps (MP-3, Eyela Microtube Pump, Tokyo Rika Kikai Co., Tokyo) via silicone tubing (2.5 mm inside diameter and 5 m length) by which pulsed flow was levelled. The reference solution was similarly introduced to R. Both tubings were held in the water bath until thermal equilibrium. The flow rate in g min^{-1} of each solution was determined by measuring the mass decrease at some time interval and converted to cm^3 min^{-1} with the observed density of solutions, if necessary.

2.3. Procedure

Two vessels of S and R were fixed in the water bath, which was then filled with the necessary amount of water. The temperature, to be controlled at 25.0°C, was set on the control panel and the temperature controller was started. At first, water was sent to all the flow paths of S and R to measure the flow rate. Then the heat exchange constant α of S was adjusted to the time constant of an analog computation circuit $(R_2C_2)^{-1}$. Actually, the variable resistor was turned on the panel of an analog computation circuit, so that an E_0–t record or a Q–t record by electric heating might be composed of three straight lines or pre-heating baseline, heating period and holding-Q period. Then, after water in the vessel was removed, each reaction solution was introduced to S and chemical oscillations were started. Calorimetric and potentiometric records were started as Q–t and E–t curves, respectively, on the Y–t recorder.

3. Results and discussion

Prior to experiments of chemical oscillation reactions, a reference substance to be introduced to the vessel R was selected. The following four pairs of liquid, water–water, 0.400 M H_2SO_4–water and H_2SO_4–0.400 M H_2SO_4 and a model solution–water were sent to vessels, S and R. respectively. The model solution was composed of 0.800 M H_2SO_4, 0.600 M MA and 0.280 M $KBrO_3$. Joule heat of 50–100 J was released from the heater element installed in S to measure the heat correction value h in J cm^{-1} which means the relation between the known heat effect and the output voltage on the Y–t recorder. The each standard deviation (SD) of five runs was less than 0.65% in every four pairs and overall SD of the observed h was also 0.29%. Therefore, water was used as the reference material for simplicity, economic reasons and pollution.

In a CSTR of flow type, oscillation aspects of BZ reactions may largely be influenced by residence time τ of reaction substances in the vessel. After Hudson et al. [2], τ was defined as the ratio of the vessel volume V to flow rate v. In the assembled calorimeter, the effective volume was observed to be 50.86 cm^3 for S and 50.64 cm^3 for R. The flow rate to S, v_s, was expressed as the total of each rate observed at three component paths which were composed of v_{s1} for $KBrO_3$ in H_2SO_4, v_{s2} for MA in H_2SO_4 and v_{s3} for Ce(IV) salt in H_2SO_4.

Almost the same conditions as Hudson et al. [2] were selected in this work for the sake of comparison, the concentrations of each substance being 1.00 mM for Ce(IV) salt, 0.300 M for MA, 0.140 M for $KBrO_3$ and 0.200 M for H_2SO_4. The chemical oscillations in 26 runs were observed in the range of v_s from 1.02 to 22.23 g min^{-1} or from 3098 to 142 s in τ. Experiments of the batch type or at $v_s = 0$ were also carried out for comparison. Typical Q and E curves against t are shown as A and B in Fig. 2. respectively, where v_s in a, b and c was observed to be 1.50 ± 0.03, 7.96 ± 0.03 and 21.00 ± 0.03 g min^{-1}, respectively, and τ in a, b and c was calculated to be 2107, 397 and 150 s, respectively, by using a density of 1.036 g cm^{-3} measured for the reaction solutions. The high period of E or the decreased period of bromide ions was prolonged with v_s. Plots of Q in J and cycle T_c or the distance between two peak maxima in E versus t curves in s at every oscillation against τ are shown in A and B of Fig. 3a, respectively. Q in curve A was monotonously decreased with τ, but as for T_c there was a maximum of 744.7 s as the mean of three runs at $\tau = 1053$ s or $v_s = 3.00$ g min^{-1}.

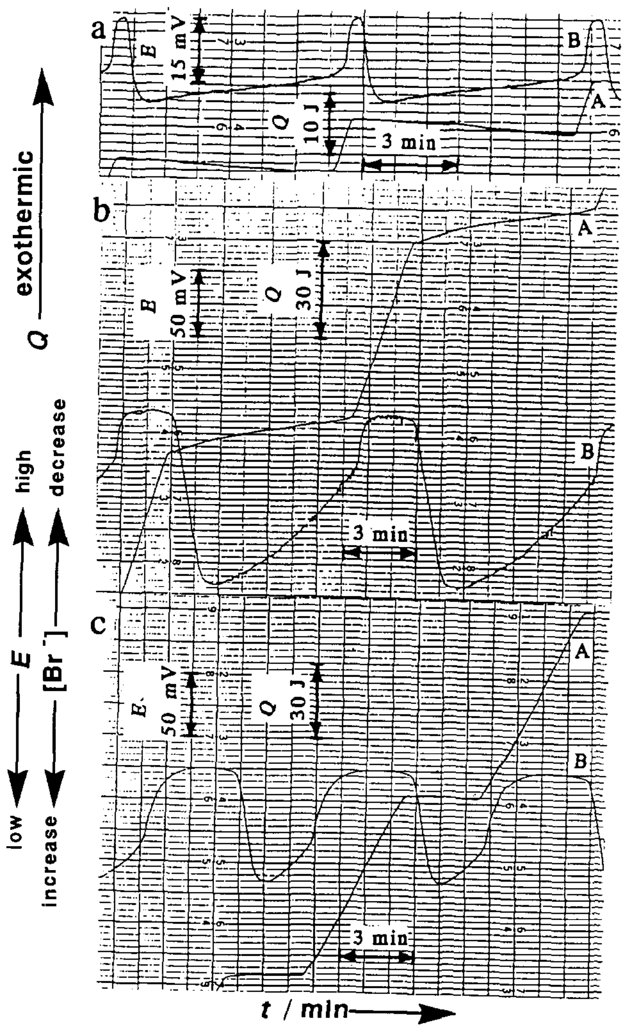

Fig. 2. The effect of τ or v_s to Q and E in every oscillation against t at $[H_2SO_4] = 0.200$ M, $[KBrO_3] = 0.140$ M, [MA] = 0.300 M and [Ce(IV) salt] = 1.00 mM: (A) Q versus t; (B) E versus t; (a) $\tau = 2107$ s or $v_s = 1.45$ cm^3 min^{-1}; (b) $\tau = 397$ s or $v_s = 7.69$ cm^3 min^{-1}; (c) $\tau = 150$ s or $v_s = 20.28$ cm^3 min^{-1}.

The quantitative repeatability in Q and E versus t curves was not so good, but the more general expression Q_{osc} was proposed from the observed results involving heat evolved in one cycle Q, flow rate v_s, cycle T_c, vessel volume V and the concentration of bromate introduced according to the custom of a batch system as J dm^{-3} l mol^{-1} of $KBrO_3$), which may be almost the same as the notation used by Roelofs [7]. Plots of Q_{osc} against τ shown in Fig. 3b were fitted by $Q_{osc} = -54.79 \pm 61.04 \log(\tau)$, for which a correlation coefficient was not so good as 0.833. The infinity in τ may correspond to a batch examination. However, it was difficult to compare numerically the Q_{osc} extrapolated to

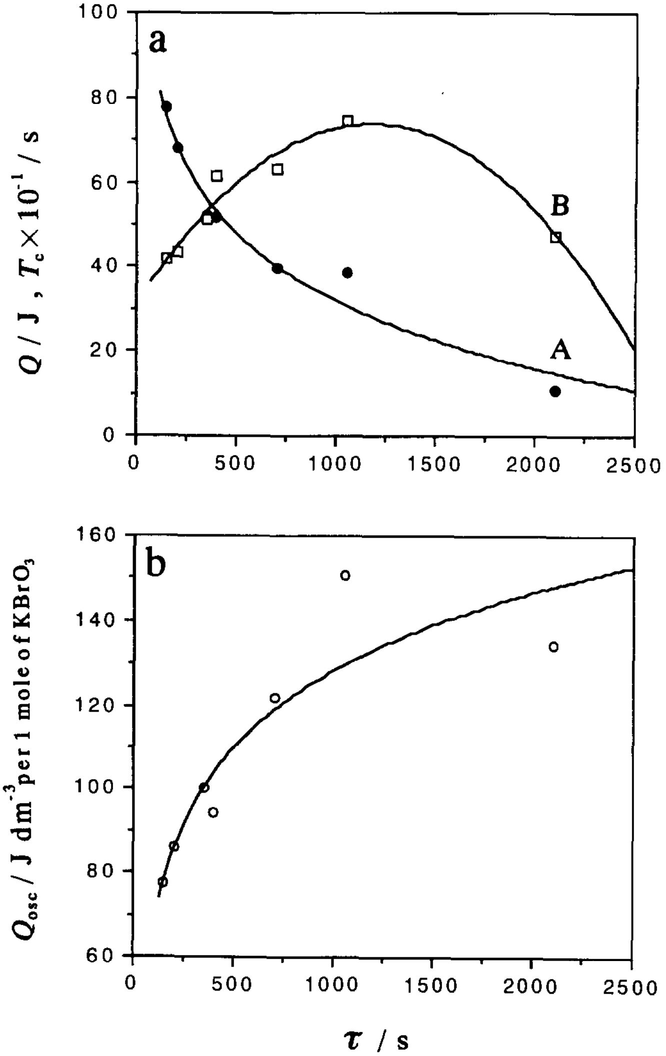

Fig. 3. Plots of Q in J and T_c in E versus t curves in s in every oscillation against τ in s observed in the same solution as in Fig. 2: (a) (A) Q versus τ and (B) T_c versus τ; (b) Q_{osc} versus τ.

infinity in τ with those by a batch system and the literature value [7], owing to the differences in dimension, such as the residence time.

On the other hand, Hudson et al. [2] used a reaction vessel of 25.4 cm^3 in volume to which the flow rate via three flow paths was in the range from 2.91 to 5.42 cm^3 min^{-1} or from 524 to 281 s in τ for 13 measurements of E versus t curves. Moreover, vessel volume and flow rate of Blittersdorf et al. [3] were 10.8 cm^3 and 2.26 cm^3 min^{-1}, respectively, with four flow paths. The stirring rate was about one half and the vessel volume was roughly twice as large in contrast to those by Hudson et al. [2]. The reasons are not

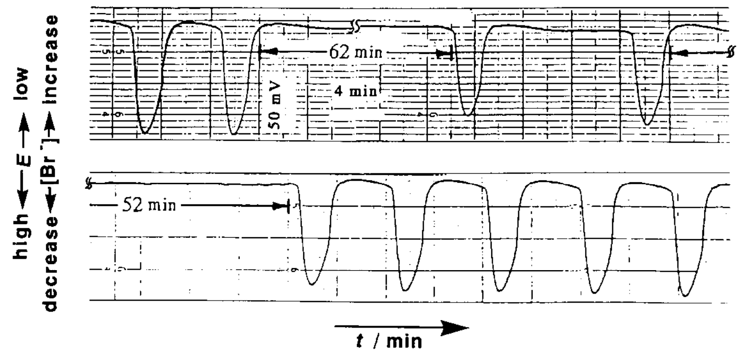

Fig. 4. The E versus t curve at small τ of 144 s or large v_s of 21.15 cm^3 min^{-1} observed in the same solution as in Fig. 2.

clear, but such complicated waves as periodic oscillations with multiple peaks were not observed in E versus t curves, as shown in Fig. 2B, although the ranges of τ reported in the literature [2,3] were covered in this study. At a large flow rate of 21.91 g min^{-1} or at short τ of 144 s, the oscillation of E against t shown in Fig. 4, in which long time intervals without any oscillation were omitted, was very irregular in frequency, but good repeatability was maintained in the wave form and the potential difference in every cycle. The start-and-stop triggers of oscillation may be affected by some unknown and delicate factors.

At one half concentration in the experiments shown in Figs. 2 and 3, any chemical oscillation was not found. When each component was concentrated twice, such irregular oscillations in both amplitude and cycle as shown in Fig. 5 were observed at τ of 1053 s.

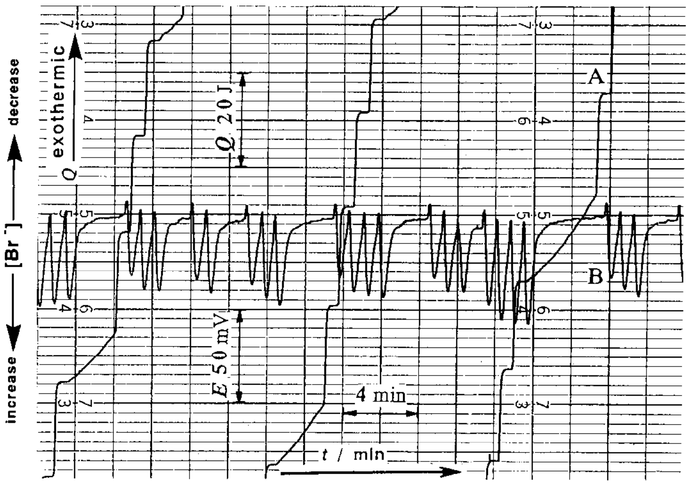

Fig. 5. Q and E against t at [H_2SO_4] = 0.400 M, [$KBrO_3$] = 0.280 M, [MA] = 0.600 M and [Ce(IV) salt] = 2.00 mM at τ = 1053 s or v_s = 2.90 cm^3 min^{-1}: (A) Q versus t; (B) E versus t.

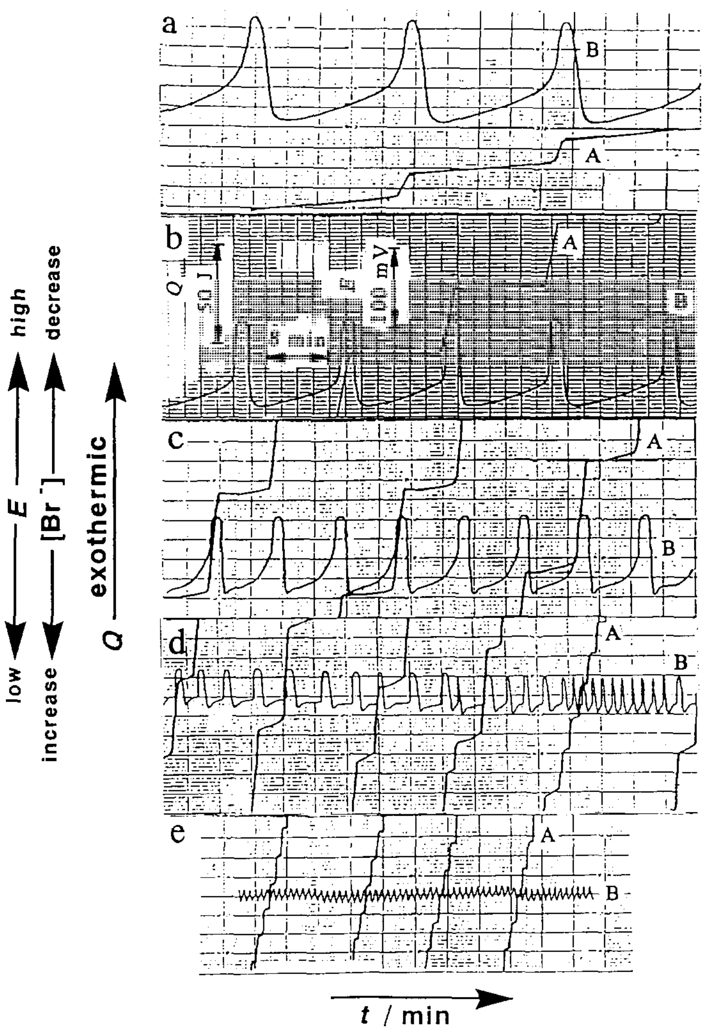

Fig. 6. The effect of concentration of sulfuric acid on Q and E against t at τ = 1053 s or v_s = 2.90 cm^3 min^{-1} in [KBrO$_3$] = 0.140 M, [MA] = 0.300 M and [Ce(IV) salt] = 1.00 mM: (A) Q versus t; (B) E versus t; (a) 0.100 M; (b) 0.200 M; (c) 0.400 M: (d) 0.600 M: (e) 0.800 M.

The trail of Q shown as A was ahead of the E trail shown as B, the difference of the two pen positions on the Y–t recorder being 3 mm in practice. In the heat exchange calorimeter, the chemical oscillation reactions may take place actually within a narrow temperature range of ±0.1°C or less, which was decided by the constancy of the temperature of the bath water. The irregular oscillations shown in Fig. 5 might come from chemical reactions, not from the erroneous measurements. The decreasing period in bromide ions also corresponded to the heat evolving period. The irregular oscillation was considered to

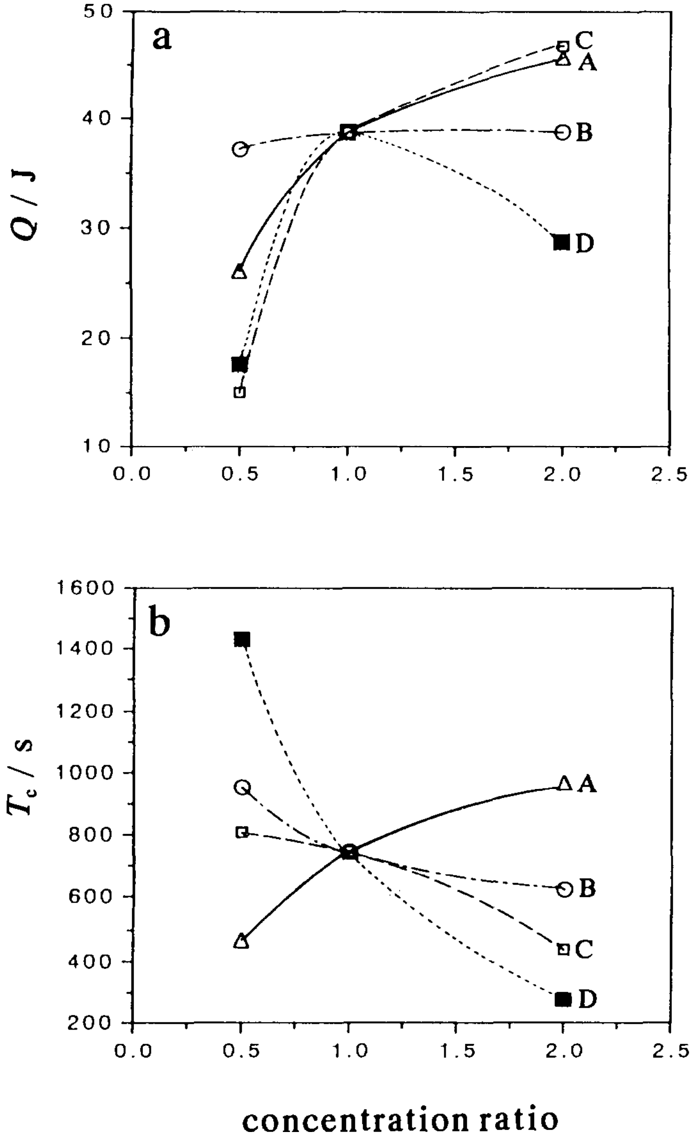

Fig. 7. Effect of concentration ratio (CR) of each component on Q and T_c at $\tau = 1053$ s or $v_s = 2.90$ cm^3 min^{-1}: (a) Q versus CR; (b) T_c versus CR; (A) variation in Ce(IV) salt; (B) variation in MA; (C) variation in $KBrO_3$; (D) variation in both $KBrO_3$ and Ce(IV) salt.

be chaotic from preliminary Lorenz plots by using the amplitude of the E versus t curve in Fig. 5. However, the detailed analyses will be discussed separately.

In the FKN scheme to explain the oscillation mechanism of BZ reactions [9] which is accepted by many researchers, the significance of the acid concentration might not be discussed. However, the acid solution should naturally be necessary for stable redox re-

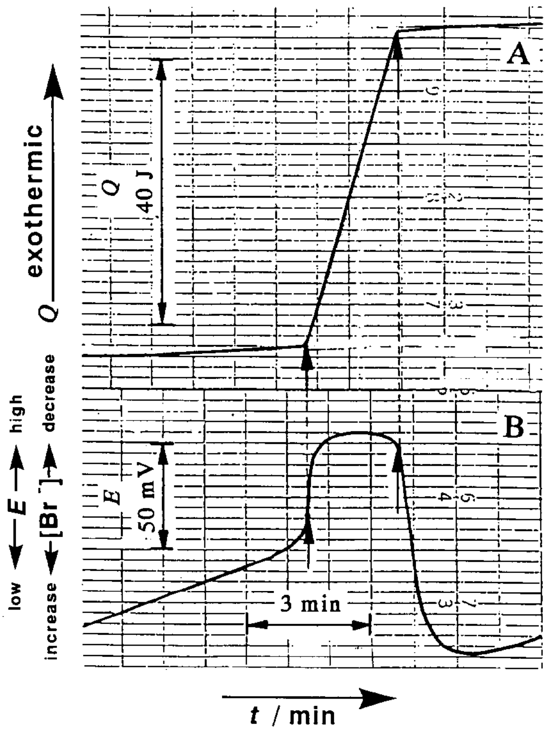

Fig. 8. Relation of heat evolution period and E versus t curve in one cycle oscillation observed in the same solution as in Fig. 2 at τ = 416 s or v_s = 7.43 cm^3/min; (A) Q versus t; (B) E versus t.

actions of bromate ions. The oscillation behavior was largely dependent upon the acid concentration. Typical results observed in several solutions different in sulfuric acid concentrations are shown in Fig. 6 for Q (A)and E (B), where b was observed at τ of 1053 s in the same solution as in Figs. 2–4. The sulfuric acid concentrations in Fig. 6a, c, d and e were 0.5, 2, 3 and 4 times, respectively, as large as that in Fig. 6b. Plots of Q in every oscillation against the concentration ratio of sulfuric acid (CR) showed a maximum of 68.5 J at CR = 2 or [H_2SO_4] = 0.400 M. In Fig. 6d or [H_2SO_4] = 0.600 M, the oscillations in E and Q were irregular and Q fluctuated between 16 J and 60 J. On the other hand, the same plots of cycle T_c versus CR were almost monotonously decreased and expressed as $T_c = 1428.3–677.3(CR) + 85.98(CR)^2$ with a correlation coefficient of 0.967 or T_c = 781.9–1195 log(CR) with a correlation coefficient of 0.972. The oscillation cycle was largely decreased with increase in the sulfuric acid concentration. The situation was almost the same as the batch runs.

Oscillation profiles of Q and E against t were recorded by changing the concentration ratio of each component at v_s = 3.00 ± 0.03 g min^{-1} or T = 1053 s. Q and T_c are plotted in Fig. 7a,b, respectively. In practice, the crossing points in Fig. 7a and b were obtained from the experiment of Fig. 6b. In curves A, B, C and D in Fig. 7, related points of the

Ce(IV) salt, MA, bromate and both bromate and Ce(IV) salt were connected by freehand, respectively. As shown by Fig. 7a, Q in J was not affected by changing the concentration of MA. Increase in the concentration ratio of Ce(IV) salt and bromate shown by curves A and C, respectively, in Fig. 7a increased Q in every oscillation. Unexpectedly, however, a simultaneous increase in both Ce(IV) salt and bromate decreased Q at the same concentration of sulfuric acid. The situation was not the same as T_c in Fig. 7b except for curve A. Curve D in Fig. 7b decreased monotonously in contrast to curve A. It may be difficult to explain the relation of Q and T_c.

Stable chemical oscillations were observed in the same solution as in Figs. 2–4 at $v_s = 7.60$ g min^{-1} or $T = 416$ s and one cycle in Q and E versus t curves is shown in Fig. 8A and B, respectively. The exothermic period was indicated by two arrows in curves A and B after correction of the pen position, which corresponded to a low period of bromide ions. The same results were also obtained by batch runs with the system assembled in the study. However, in the batch system, malonic acid is decomposed to formic acid and carbon dioxide with the progress of reactions. Therefore, a more constant duration of oscillations may be obtained from results of the CSTR. In spite of experimental mode such as flow and batch, the production period of bromide ions involving malonic acid in process C of the FKN scheme [9] may be the most reasonable time for the heat evolution. Taking the discussion by Lamprecht [6] into consideration, most of the heat may be evolved in the reaction for producing bromomalonic acid in the FKN model. For more detailed discussions to make the cause of heat evolution clear, calorimetry of a minimal oscillation reaction by using bromide as a reductant is recommended [10].

Acknowledgements

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