

Caloric behaviour in the induction period of Belousov–Zhabotinskii reactions monitored by heat exchange calorimetry of batch type and the simultaneous estimation of the potentiometric aspect

Junko Kawahito ^a and Shuko Fujieda ^b

^a *The Doctoral Research Course in Human Culture, Ochanomizu University, Bunkyo-ku, Tokyo 112 (Japan)*

^b *Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112 (Japan)*

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Abstract

The induction period of the Belousov–Zhabotinskii (B–Z) reactions which occur in an aqueous solution composed of potassium bromate, sulphuric acid, malonic acid and ammonium cerium(IV) sulphate was studied in the same reaction by heat exchange calorimetry of batch type and potentiometry. The sample and reference vessels were fixed differentially in a home-made heat exchange calorimeter in a temperature-controlled water bath. The heat evolved in the vessel was exchanged freely with the surrounding water. The rate of heat evolution q and the total heat effect Q were estimated by the analogue treatments of electrical signals observed as temperature changes via thermistors placed in each vessel. A standard potentiometric cell was also present in the water bath in order to obtain simultaneously the potential difference E which reflects the bromide concentration in the reaction. When fine crystals of the cerium(IV) salt are added to start the B–Z reaction, a small endothermic peak is observed in the q versus t curve, followed by large exothermic double peaks. In the induction period, only the smaller change is observed in the potentiometry. The Q values in the induction period depend significantly upon the initial concentrations of KBrO_3 and H_2SO_4 in the solution, in contrast to those of malonic acid and cerium(IV) salt. Several minor fluctuations in Q and the E versus t curves are observed in the induction period of dilute KBrO_3 or H_2SO_4 solution. The ΔH values in the induction period were also estimated in several different concentrations of the initial constituents.

INTRODUCTION

The Belousov–Zhabotinskii (B–Z) reaction is the most typical of chemical oscillations in non-equilibrium systems. The reaction which was

Correspondence to: S. Fujieda, Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan.

discovered by Belousov [1] and then developed by Zhabotinskii [2], has also been used in chemical demonstrations. However, the reaction mechanism is very complicated. Field and coworkers proposed the oscillation mechanism known as the FKN scheme [3]. The oscillation was explained as a repetition from Process A to Process C.

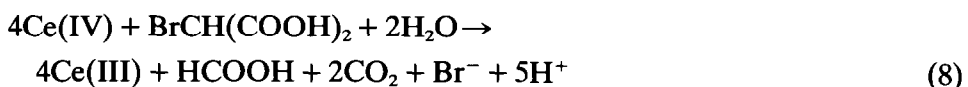
Process A



Process B



Process C



A large number of reports have been published on B-Z reactions, but they were studied mainly by means of spectrophotometry and potentiometry. Unfortunately, calorimetric data are scarce [4-7].

The calorimetric and potentiometric data of the B-Z reactions of KBrO_3 , H_2SO_4 , malonic acid and $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ were estimated simultaneously in a previous report [8], in which heat exchange calorimetry of batch type [9] was also used. The sample and reference vessels were fixed differentially in the temperature-controlled water bath. The heat evolved in the vessel was exchanged freely with the surrounding water. The thermal regime in the vessel was expressed by the Newtonian cooling equation, $dT/dt = (q/C) - \alpha T$, where T is temperature, t time, q rate of heat evolution, C effective heat capacity and α a constant to express heat exchange efficiency. In practice, the temperature θ observed via a thermistor installed in each vessel may include a delay in response time. The relationship between T and θ may be expressed in a simple differential equation, such as $d\theta/dt = \beta(T - \theta)$, where β is a constant for the extent of the delay. From the electrical signals corresponding to θ , the q and the total heat effect Q were obtained by means of an analogue

computation circuit. A standard potentiometric cell was also incorporated into the vessel in the heat exchange calorimeter. During the calorimetric measurements of chemical oscillation reactions, the potential difference of the bromide ions E between the Ag/AgBr electrode and the reference electrode was also observed. The estimated values of q , Q and E in the oscillation period were related to the FKN scheme.

Experiments of batch type may provide much information on the induction period of chemical oscillation reactions. In addition, bifurcation phenomena from the induction period to the oscillation period may also be observed [10, 11], even though the mechanism may not be explicit.

In the present report, the induction period in the B–Z reactions was studied from the q and Q values obtained by heat exchange calorimetry of batch type and from E obtained in the same run using the potentiometric cell. The sample solutions were composed of potassium bromate, sulphuric acid, malonic acid and ammonium cerium(IV) sulphate. Because the Q in the induction period depended on the initial concentrations of KBrO_3 or H_2SO_4 , as demonstrated in our previous study [8], the initial content of KBrO_3 or H_2SO_4 was decreased to the threshold of oscillation. The q , Q_{ind} and E in the induction period were observed at $25.0 \pm 0.1^\circ\text{C}$, and the corresponding ΔH_{ind} per mole of initial potassium bromate was also estimated from Q_{ind} .

EXPERIMENTAL

Reagents

All the reagents were from Wako Chemicals Co., Tokyo, of guaranteed grade, used without further purification. The aqueous chemical oscillation system was composed of KBrO_3 , H_2SO_4 , $\text{CH}_2(\text{COOH})_2$ and $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ in different initial concentrations. The initial concentration of the components was in the range 5.00 mM to 0.100 M, 70.0 mM to 0.900 M, 20.0 mM to 0.500 M and 0.600 to 4.00 mM, respectively. Deionized water was used after distillation as usual.

Apparatus

The heat exchange calorimeter, whose essential parts were similar to those reported previously [8], was assembled including the potentiometric cell. A glass box of $21 \times 30 \times 27 \text{ cm}^3$ in size was used as the water bath, six surfaces of which were covered with 5 cm thick Styrofoam insulator boards, and was usually filled with about 12 dm^3 of water. A hand-made frame was used to fix sample and reference vessels in the water bath [12]. The temperature of the bath water was controlled by an 8-bit microcomputer (M5, SORD Co., Tokyo, conducted by Z-80, Zilog) within the

narrow range of $\pm(3-4) \times 10^{-4}$ K using a method previously reported [13]. The temperature in the vessels was observed with the thermistors installed in each vessel (type MB, Takara Kogyo Co., Tokyo), transferred to electrical signals via a Wheatstone bridge and a preamplifier (PM-17A, Toa Dempa Kogyo Co., Tokyo) followed by calculations of Q and q involving the analogue computation circuit [8].

A silver rod, 2 mm in diameter, as short as possible to prevent heat leakage, was installed in each of the sample and reference vessels, for the Ag/AgBr electrodes. At the same time, one end of the salt bridge containing approx. 2% potassium nitrate in agar was installed in the sample vessel; and another end of an identical salt bridge was installed in the reference vessel to compensate for the effective heat capacity. The potential difference E relative to the concentration of bromide ions was observed against a commercially available saturated Ag/AgCl electrode (HC-205C, Toa Dempa Kogyo Co., Tokyo) which served as a reference electrode. The observed Q_{ind} , q and E were recorded on a strip chart recorder (R-02, Rika Denki Co., Tokyo).

Procedure

Aliquots of 50.0 g of the aqueous mixture of potassium bromide, sulphuric acid and malonic acid were weighed and placed in the sample and reference vessels, which were then fixed in the frame in the water bath. The temperature control system of the bath water was started. When temperature equilibrium was attained in the water bath and the electrical circuits and devices had warmed up after a time lapse of 30–40 min, the time constants of the analogue circuit were adjusted to those of the calorimeter by turning the variable resistors in the analogue circuit in the process of electrical heating. After the caloric calibration by the evolution of joule heat, the weighed crystals of Ce(IV) salt, which were finely powdered so as to dissolve quickly, were thrown in the sample vessel from outside the water bath without removing the cover board, and the B–Z reaction was started. Each output voltage of the operational amplifiers was recorded as q and Q_{ind} against time, and the difference between the two electrodes E was also recorded as the potential difference.

RESULTS AND DISCUSSION

The oscillation behaviour of a B–Z reaction in the critical concentration may depend in particular upon the stirring effect of the reaction solution. In the present study, the rotation rate of the iron bar in each vessel was virtually fixed to about 330 per min^{-1} . The initial concentrations for potassium bromate, sulphuric acid, malonic acid and ammonium

cerium(IV) sulphate were 0.0700 M, 0.500 M, 0.300 M and 2.13 mM, respectively, for stable oscillation and labelled as typical initial concentrations in this report. All the solutions were used in the sample and reference vessels were weighed as 50.00 ± 0.01 g. The observed density of the typical solutions was 1.0348 ± 0.0003 g cm⁻³ and was used in the calculations of volume.

Typical curves of q versus t measured by the home-made heat exchange calorimeter of batch type and of E versus t in the same run are shown in Fig. 1. The records in the time lapse of 40–50 min in the oscillation period were omitted between (A) and (B) in Fig. 1 for simplicity. The start of the reaction is shown by an upward arrow in Fig. 1. The heat of solution of the cerium(IV) salt to water was endothermic, the ΔH value being 11.2 ± 0.1 kJ mol⁻¹ [8]. Because the observed total heat of solution was so small, -1.14 ± 0.01 J, the record was magnified as I in Fig. 1(C). The following two steps of heat evolutions, II and III, were measured as shown in q in Fig. 1(A). Before step II had completely returned to the base line, step III started.

The Q_{ind} observed as output voltage of the analogue computation circuit, which is not shown in Fig. 1, was fairly large and estimated to be 123.0 ± 0.6 J, as a mean of 8 runs with the standard deviation. The ΔH was estimated to be -36.37 ± 0.19 kJ per mole of initial potassium bromate. Körös et al. [4] also reported the calorimetric measurements in the induction period, in which an aqueous catalytic solution was added to start the reaction. The reported ΔH of -29.1 kJ per mole of initial potassium bromate was observed at the initial concentrations of 0.100 M, 0.5 M, 0.40 M and 1.15 mM of potassium bromate, sulphuric acid, malonic acid and cerium(IV) salt, respectively. In the most similar solution, in the

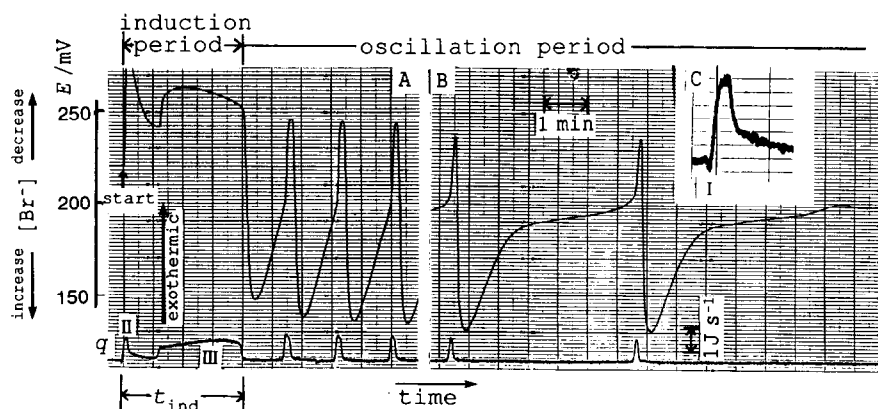


Fig. 1. Typical calorimetric and potentiometric curves for the B-Z reaction in the solution composed of KBrO₃ (0.0700 M), H₂SO₄ (0.500 M), CH₂(COOH)₂ (0.300 M) and Ce(IV) salt (2.13 mM) at 25°C: q , rate of heat evolution; E , potential difference of [Br⁻] versus the reference electrode.

present work, containing 0.100 M of potassium bromate, 0.500 M of sulphuric acid, 0.300 M of malonic acid and 2.13 mM of cerium(IV) salt, which has corrected for the heat of solution of the cerium(IV) salt, the ΔH at $25.0 \pm 0.1^\circ\text{C}$ was estimated to be -26.77 ± 0.69 kJ per mole of initial potassium bromate.

The total heat effect in the induction period Q_{ind} depended significantly upon the initial concentrations of potassium bromate and sulphuric acid [4, 8]. The critical concentration of sulphuric acid to start the oscillation was estimated to be 0.150 M from potentiometric data of bromide ions. Therefore, in the present report, Q_{ind} and E were observed in more dilute regions than the critical concentration of sulphuric acid. The two curves shown in Fig. 2(A) were observed in 8.00 or 10.0 mM of $[\text{KBrO}_3]_{\text{init}}$ and with the other components in the typical concentrations. A small decrease in E or an increase in bromide concentration was observed about 9 min after the start. Q_{ind} was increased by a step, and then a small change was observed. In the solution containing a $[\text{KBrO}_3]_{\text{init}}$ of 20.0 mM or 24.0 mM, a peak in E was observed (the downward arrow) and, in contrast the curve in Fig. 2(A), there was no subsequent small decrease in E (Fig. 2(B)). The corresponding two large and small peaks followed. In the very dilute solution of $[\text{KBrO}_3]_{\text{init}}$ in Fig. 2(A), the production of bromine compounds necessary for an oscillation reaction was not possible, but this may be possible in Fig. 2(B), where the concentration of bromide ions has increased. This may be considered as a single oscillation. In the solutions with higher $[\text{KBrO}_3]_{\text{init}}$, the oscillation became stable, with an increase in oscillation number and magnitude. With $[\text{KBrO}_3]_{\text{init}}$ of 0, 5.00, 8.00, 10.0, 20.0, 24.0, 28.0 and 41.0 mM, the following Q_{ind} values (J) shown as a mean of several runs and the standard deviation (after \pm), and the estimated ΔH_{ind} values (kJ per mole of initial potassium bromate), in

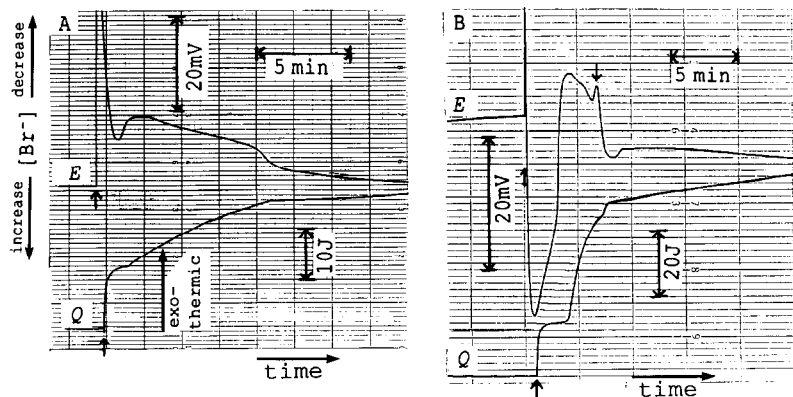


Fig. 2. Calorimetric and potentiometric curves in the dilute solution of KBrO_3 , other components being included in the same concentration as in Fig. 1: (A) 8.00 mM; (B) 20.0 mM. Q is the total heat effect.

parentheses, were observed: 13.14 ± 0.02 , 14.04 ± 0.25 (-58.1 ± 1.0), 26.84 ± 1.04 (-69.3 ± 2.7), 33.99 ± 1.08 (-70.3 ± 2.2), 47.64 ± 2.42 (-49.2 ± 2.5), 50.51 ± 2.06 (-43.5 ± 1.8), 54.38 ± 2.25 (-39.5 ± 1.7) and 70.74 ± 1.03 (-35.7 ± 0.5), respectively. For the first two points, the heat evolution shown as III in Fig. 1 was not found. To indicate the whole relationship, including the more stable region, plots of Q_{ind} versus $[\text{KBrO}_3]_{\text{init}}$ are shown in Fig. 3, curve A. The standard deviation is shown by the length of the bar on each point. Solid symbols are used for the concentrations at which oscillation is found; open symbols are used when oscillation is not found. A partly linear relation between Q_{ind} and $[\text{KBrO}_3]_{\text{init}}$ was observed, but regularity was not found as a whole.

The chemical oscillation only proceeds in acidic solution. Therefore, a dilute solution of sulphuric acid should include malonic acid. With a $[\text{H}_2\text{SO}_4]_{\text{init}}$ of 0.0700 M with the other components being in the typical concentrations, plots of Q_{ind} and E against t shown in Fig. 4(A) were obtained; those are essentially the same as those in Fig. 2(A). Almost the same curves were also obtained with $[\text{H}_2\text{SO}_4]_{\text{init}} = 0.150$ M, the critical concentration determined in the previous study [8]. However, in the case of $[\text{H}_2\text{SO}_4]_{\text{init}} = 0.160$ M, as shown in Fig. 4(B), several small oscillations were observed on the Q and E curves with good reproducibility. After the oscillations, E decreases as shown in Figs. 2(A) and 4(A) and then no further oscillations were found. The same result was observed with 0.180 M $[\text{H}_2\text{SO}_4]_{\text{init}}$. As expected, more concentrated solutions of $[\text{H}_2\text{SO}_4]_{\text{init}}$ always displayed explicit oscillations.

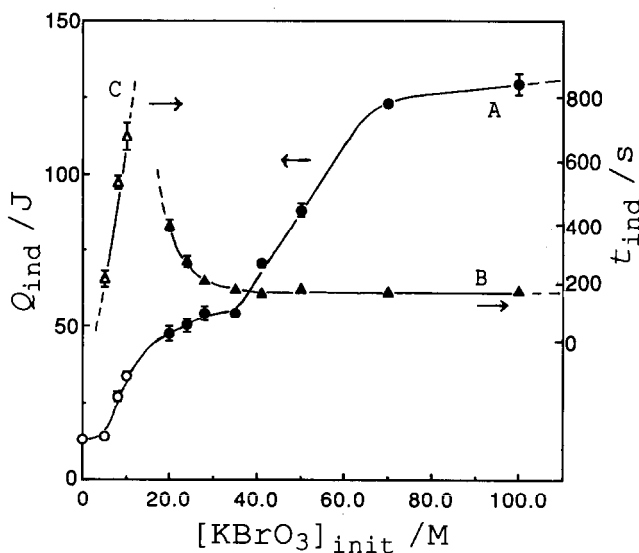


Fig. 3. Plots of Q_{ind} and t_{ind} in the induction period against $[\text{KBrO}_3]_{\text{init}}$: Q_{ind} , total heat effect evolved; t_{ind} , duration time of induction period. Solid symbols for appearance of oscillation and open symbols for no oscillation reaction.

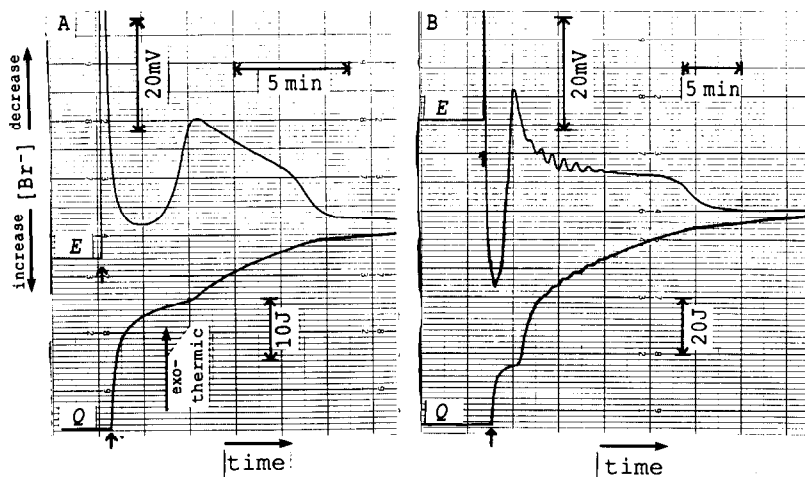


Fig. 4. Calorimetric and potentiometric curves in the dilute H_2SO_4 , other components being in the same concentration as in Fig. 1: (A) 70.0 mM; (B) 0.160 M.

Plots of observed Q_{ind} versus $[\text{H}_2\text{SO}_4]_{\text{init}}$ are shown in Fig. 5, curve A. At each point, the mean of 4–10 runs and the standard deviations were used in the same manner as in Fig. 3. With $[\text{H}_2\text{SO}_4]_{\text{init}}$ values of 0, 0.0700, 0.150, 0.160 and 0.180 M, oscillation was not found, as indicated by open marks in Fig. 5, and the Q_{ind} (J) and ΔH_{ind} (kJ per mole of initial potassium bromate), in parentheses, were 17.0 ± 0.03 (-4.868 ± 0.010), 31.7 ± 1.61 (-9.07 ± 0.46), 58.7 ± 2.86 (-16.9 ± 0.8), 68.0 ± 2.74 (-19.6 ± 0.8) and 71.2 ± 3.9 (-20.6 ± 1.1), respectively. The relationship between

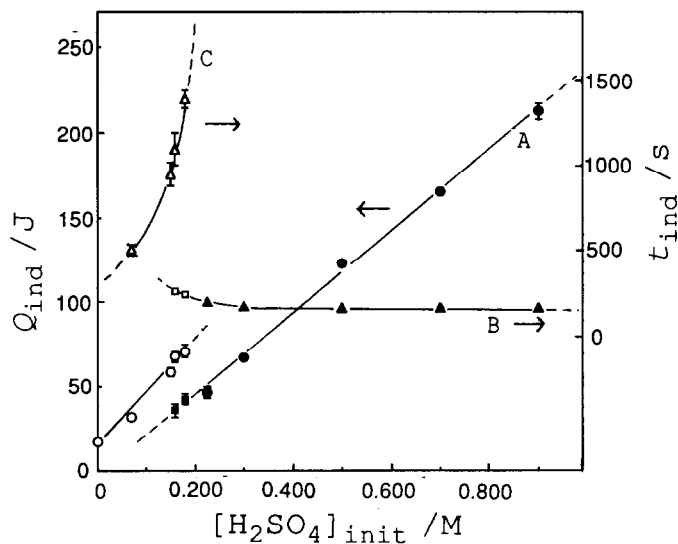


Fig. 5. Plots of Q_{ind} and t_{ind} in the induction period versus $[\text{H}_2\text{SO}_4]_{\text{init}}$, as in Fig. 3.

Q_{ind} and $[\text{H}_2\text{SO}_4]_{\text{init}}$ was linear. With 0.160 M and 0.180 M $[\text{H}_2\text{SO}_4]_{\text{init}}$, the total heat effect (J) and ΔH (kJ per mole of initial potassium bromate) prior to several oscillations were 36.0 ± 3.64 (-10.4 ± 1.1) and 42.8 ± 3.32 (-12.4 ± 1.0), respectively. These data are shown as squares in Fig. 5(A) and are placed on the line indicating oscillation.

The induction period t_{ind} , shown in Fig. 1 and defined as the time from the start of reaction to the beginning of the first oscillation was discontinuous in the critical region, as shown as B and C in Fig. 3. In the non-oscillation region shown as C in Fig. 3, the continuation time of the reaction was prolonged with increase in $[\text{KBrO}_3]_{\text{init}}$. However, as shown in curve B in Fig. 3, t_{ind} generally decreased with the appearance of the oscillation and with an increase in $[\text{KBrO}_3]_{\text{init}}$. The same situation was also found in the plots of q versus t shown in Fig. 6. With a $[\text{KBrO}_3]_{\text{init}}$ of 35.0 mM, the t_{ind} was lengthened a little as shown in Fig. 6(A), but t_{ind} in Fig. 6(B)-(D) were almost the same. Almost the same discontinuity of t_{ind} was observed in the case of sulphuric acid shown as curves B and C in Fig. 5. The observed plots of q versus t are shown in Fig. 7. The curves of q versus t for malonic acid and cerium(IV) salt at the initial concentrations for which oscillations were observed are shown in Figs. 8 and 9, respectively; these are considerably different from those of potassium bromate and sulphuric acid, especially in the duration of the induction period, or more exactly, in step III. Figure 7(D) and (E) the initial parts of Figs. 6(D), 8(D) and 9(D) are reduced in the ordinate to the scale of 1 to 3.47.

The observed Q_{ind} corresponding to the peak area integrated on the q vs. t curves shown in Figs. 6-9 and the ΔH_{ind} calculated from Q_{ind} are summarized in Table 1. The Q_{ind} and ΔH_{ind} values are the means of

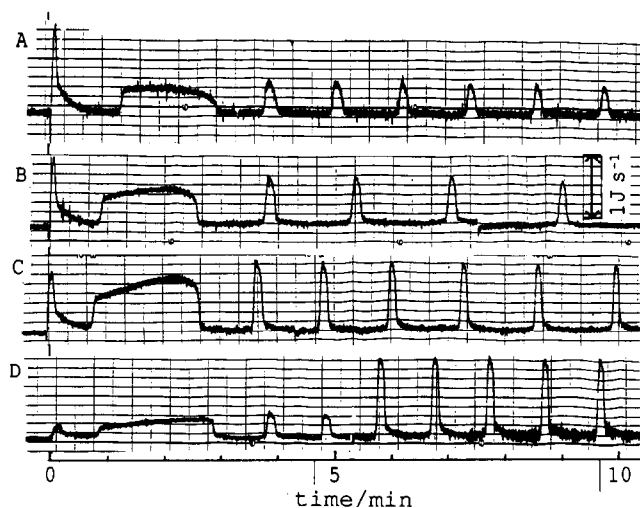


Fig. 6. Influence of the variation of $[\text{KBrO}_3]_{\text{init}}$ on the observed q plotted versus time: (A) 35.0 mM; (B) 50.0 mM; (C) 70.0 mM; (D) 100.0 mM.

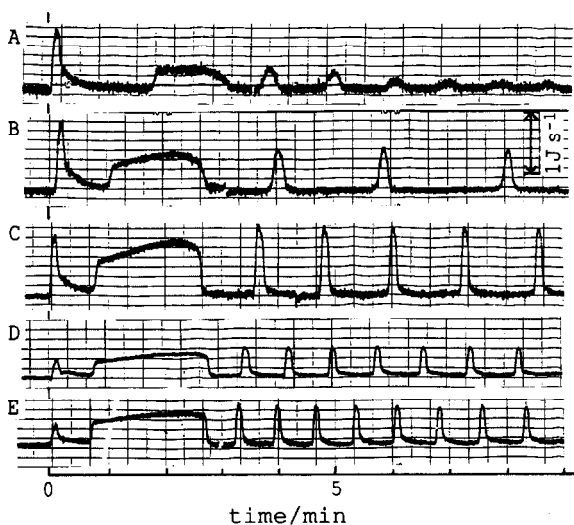


Fig. 7. Influence of the variation of $[\text{H}_2\text{SO}_4]_{\text{init}}$ on the observed q plotted versus time: (A) 0.225 M; (B) 0.300 M; (C) 0.500 M; (D) 0.700 M; (E) 0.900 M.

several runs, with the standard deviations. All the experiments were carried out in typical concentrations of the components, except with the variations of the relevant species. The ΔH_{ind} in the fourth column was expressed as kJ per mole of initial potassium bromate.

The heat evolved in steps II and III of the q versus t plots was overlapping. The higher the initial concentrations of potassium bromate, sulphuric acid and malonic acid, and the lower that of cerium(IV) salt, the greater the extent of overlap. The heat evolution of step II was observed in the solution without potassium bromate or sulphuric acid as shown in

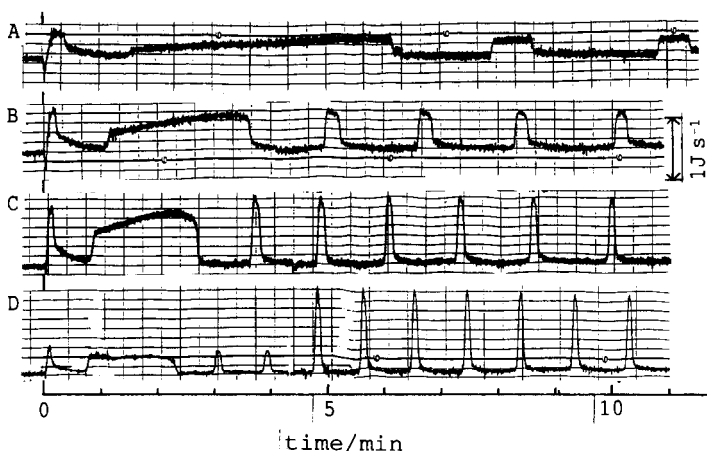


Fig. 8. Influence of the variation of $[\text{CH}_2(\text{COOH})_2]_{\text{init}}$ on the observed q plotted versus time: (A) 60.0 mM; (B) 0.150 M; (C) 0.300 M; (D) 0.500 M.

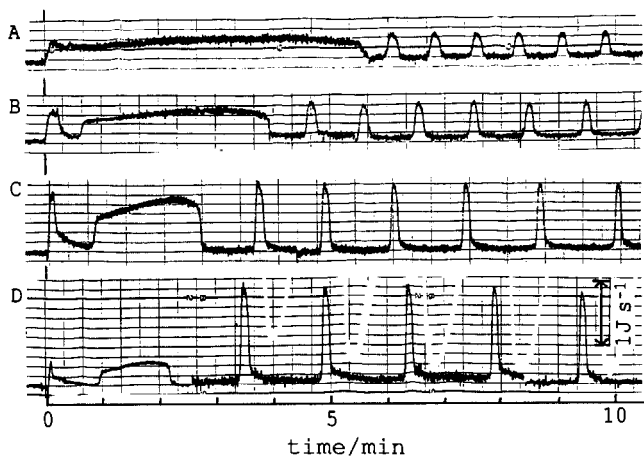


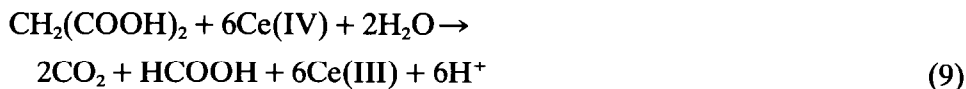
Fig. 9. Influence of the variation of $[\text{Ce(IV) salt}]_{\text{init}}$ on the observed q plotted versus time: (A) 0.600 mM; (B) 0.999 mM; (C) 2.13 mM; (D) 4.00 mM.

TABLE 1

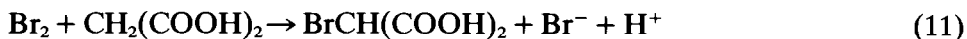
The calorimetric estimation of Q_{ind} and ΔH_{ind}

	Fig. and area	Q_{ind} (J)	ΔH_{ind} (kJ mol ⁻¹)
$[\text{KBrO}_3]_{\text{init}}$ (mM)			
35.0	6 (A)	54.3 ± 0.6	-32.13 ± 0.38
50.0	(B)	88.5 ± 2.2	-36.65 ± 0.92
70.0	(C)	123.0 ± 0.6	-36.37 ± 0.19
100.0	(D)	129.4 ± 3.3	-26.77 ± 0.69
$[\text{H}_2\text{SO}_4]_{\text{init}}$ (M)			
0.225	7 (A)	46.5 ± 3.5	-13.49 ± 1.00
0.300	(B)	67.8 ± 1.5	-19.78 ± 0.43
0.500	(C)	123.0 ± 0.6	-36.37 ± 0.19
0.700	(D)	164.9 ± 1.2	-49.43 ± 0.37
0.900	(E)	212.6 ± 5.0	-64.54 ± 1.52
$[\text{Malonic acid}]_{\text{init}}$ (M)			
0.0600	8 (A)	107.0 ± 1.6	-31.63 ± 0.48
0.150	(B)	114.9 ± 1.3	-33.97 ± 0.40
0.300	(C)	123.0 ± 0.6	-36.37 ± 0.19
0.500	(D)	133.6 ± 1.1	-39.50 ± 0.32
$[\text{Ce(IV) salt}]_{\text{init}}$ (mM)			
0.600	9 (A)	124.5 ± 3.8	-36.81 ± 1.11
0.999	(B)	122.7 ± 1.2	-36.28 ± 0.36
2.13	(C)	123.0 ± 0.6	-36.37 ± 0.19
4.00	(D)	122.8 ± 0.6	-36.31 ± 0.17

Fig. 3, curve A and Fig. 5, curve A, respectively. However, it was not observed in the absence of either malonic acid or cerium(IV) salt. The following reactions studied by Kasperek and Bruce [14] may explain the heat evolution in step II.



The rate constant of reaction (9) was reported to be $k_9 = 8.8 \times 10^{-2} \text{ s}^{-1}$ [14]. However, the maximum heat evolving rate in step III was roughly equal to that in the oscillation period. Therefore, it was considered that almost the same reaction might take place in step III as in the oscillation period. Bromomalonic acid which is necessary for reaction (8) is produced in the induction period [15]



The rate constant of reaction (11), k_{11} , was $1.3 \times 10^{-2} \text{ s}^{-1}$ [3]. The bromomalonic acid may be produced by reactions (10) and (11) [3]. The time from the start to the point of inflection at which the heat evolution in step III is greater than that in step II, was shortened with increasing initial concentrations of potassium bromate, sulphuric acid and malonic acid. However, in the case of high concentration of cerium(IV) salt, the whole induction period was shortened, the duration of step II being lengthened with increasing concentration.

As discussed previously in relation to calorimetric data [8], the induction period ended with the sudden decrease in E or increase in bromide ions, which corresponded to the Process C or reaction (8) in the FKN scheme [3]. Periodic heat evolutions in the oscillation period corresponded to the time between Process B and Process C in the FKN scheme [3] deduced from the observed q and E curves. The period with no evolving heat also corresponded to Process A. In most runs, the oscillation cycle was prolonged and the magnitude and peak height was decreased, as shown in Fig. 1.

From the FKN scheme [3] in the oscillation period, the switching from Process A to Process B indicated that the reaction of HBrO_2 with bromide ions by reaction (2) was transferred to that with bromate ions in reaction (5), owing to the decrease in the concentration of bromide ions. The starting time of reaction (5) was obtained from the ratio of the rate constants as $[\text{Br}^-]_{\text{crit}} = (k_5/k_2)[\text{BrO}_3^-]$. In the previous report [8], $[\text{Br}^-]_{\text{crit}}$ was deduced from potentiometric and calorimetric studies. A similar approach was applied to the explanation of switching in the induction period. The condition under which the reaction of malonic acid with bromine begins to dominate over the oxidation reaction of malonic acid

with cerium(IV) salt, might be expressed as $[Br_2] > (k_9/k_{11})[Ce(IV) \text{ salt}]$. The relationship corresponds to the results showing that the time from the start to the point of inflection increased with increasing concentration of cerium(IV) salt, as shown in Fig. 9.

In the concentration region where the t_{ind} was almost constant, Q_{ind} indicated clear dependence on the concentration of $[KBrO_3]_{init}$ and $[H_2SO_4]_{init}$ as shown in Figs. 3 and 5, respectively. Therefore, the elementary reaction for determining the reaction rate in the induction period may be different from the main step of heat evolution.

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