Thermochimica Acta, 183 (1991) 153-165
Elsevier Science Publishers B.V., Amsterdam

Thermal behaviour of Belousov-Zhabotinskii reactions followed by heat exchange calorimetry involving simultaneous estimation of potentiometric oscillations *

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(Received 10 September 1990)

Abstract

The chemical oscillations of the Belousov-Zhabotinskii reactions which occur in a solution composed of $KBrO_3$, H_2SO_4, $CH_2(COOH)_2$ and $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$, have been followed simultaneously by heat exchange calorimetry of a batch type and by potentiometry in order to study the relation between the thermal behaviour and the reaction mechanism. In the assembled calorimeter, the sample and reference vessels were fixed differentially in a water bath. The heat evolved in the sample vessel was exchanged freely with the ambient water whose temperature was controlled precisely. Because this reaction does not change the effective heat capacity, it was a very suitable subject for the calorimetric study. A normal potentiometric cell was also assembled in the bath to estimate the potential difference of the same reaction. The rate of heat evolved q, the total heat effect Q and the potential difference of the bromide ions, E, were measured against time t. After the start of the reaction, large Q values were measured in the induction period, in contrast to only a small change in E which increased linearly with initial concentrations of H_2SO_4 and $KBrO_3$. In the oscillation period, the amount of Q evolved in each cycle decreased exponentially with t. The measured q value depended on the initial concentrations of the components, and was compared with the values of E estimated simultaneously. The threshold value of $[H_2SO_4]_{init}$ obtained from the relation between q and E was compared with that calculated from the rate constants obtained from the literature; fairly good agreement was obtained.

INTRODUCTION

Chemical oscillations were first found by B.P. Belousov in 1951 and were reported in 1958 [1]. The Belousov-Zhabotinskii (B-Z) reaction has been

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* Paper presented at the Second Japan-China Joint Symposium on Calorimetry and Thermal Analysis, 30 May-1 June 1990, Osaka, Japan.

studied most frequently: it displays some very interesting phenomena including apparent chemical magic. The phenomenon of oscillation results from complex chemical reactions [2] and is related to chaotic phenomena. The spectrophotometry of colour changes and the potentiometry of intermediate species, which is also appropriate for reactions with no colour change, are usually used to study reaction mechanisms and the development of new chemical systems.

Several hundred reports [3–5] have been published on the subject of chemical oscillations. When the study of B–Z reactions was first developing, thermodynamic data which may provide effective and fundamental information in the investigation of reaction mechanisms were collected [6–8]. However, most calorimetric investigations were usually carried out on calorimeter systems which had been designed and assembled for a specific purpose. Therefore, only a small number of relevant calorimetric studies have been reported [9–12].

Heat exchange calorimetry was introduced by Nakanishi and Fujieda [13] and has since been developed. Chemical oscillation reactions may be suitable subjects for study by batch-type calorimetry. Because the sample volume does not change during an oscillation reaction, the calorimetric experiment does not involve a change in the effective heat capacity. Therefore the instrumentation of the calorimeter and the data handling were simplified. The sample and reference vessels were placed in a water bath. The heat evolved in the sample vessel was exchanged freely with the ambient water, even if a large heat effect was involved. Since the temperature of the bath water was controlled strictly within a narrow range, $\pm(3-4) \times 10^{-4}$ K [14], the caloric effect and thermal change in the B–Z reactions may be estimated at constant temperatures. As a method for detailed calorimetric studies of the B–Z reaction, heat exchange calorimetry may be preferred over an adiabatic method because the rate of heat evolution which is very informative in the analysis of the oscillation mechanism, is determined easily by this technique.

In practice, the reproducibility of the chemical oscillations was poor because of some delicate experimental conditions [15]. Therefore a comparison of the experimental results obtained from separate calorimetric and potentiometric runs is not recommended.

In the present work, the rate of heat evolution or the instantaneous heat evolution q, and the total heat effect Q, in the B–Z reaction were estimated by batch-type heat exchange calorimetry at 25.0 ± 0.1° C. The potentiometric measurement of the intermediate bromide ions was carried out simultaneously in the same run. The estimated thermogram and the potentiometric trace provide information on the thermal behaviour and the reaction mechanism, and their relationship; this is discussed below.

EXPERIMENTAL

Reagents

All the reagents were of guaranteed grade and were used without further purification. The chemical oscillation systems were composed of potassium bromate, sulphuric acid, malonic acid and ammonium cerium(IV) sulphate, for which the initial concentrations were in the range 0.0280–0.100 M, 0.225–0.900 M, 0.0600–0.500 M and 0.422×10^{-3}–4.00×10^{-3} M respectively. Solid cerium(IV) salt was used to initiate the oscillation reaction. As usual, deionized water was used after distillation.

Apparatus

A heat exchange calorimeter, whose fundamental concept and essential parts were almost the same as reported previously [16], was assembled as shown in Fig. 1, with the inclusion of a standard potentiometric cell, which was omitted from the figure for simplicity. About 12 dm^3 of water were used in the temperature-controlled bath, which was 27 × 30 × 27 cm in size and covered with thermal insulator boards. In the sample and reference vessels, shown as S and R respectively in Fig. 2, silver rods 2 mm in diameter, used as Ag–AgBr electrodes, and one end of the salt bridge which contains approximately 2% potassium nitrate in agar, were installed to compensate for the effective heat capacity. The silver rod was made as short as possible to minimize heat leakage and heat capacity. The thermistors installed in the S and R vessels (MB, Takara Thermistor Instrument Co. Ltd., Tokyo) had *B* constants of 3377.5 and 3377.7 and resistances of 5.639 and 5.625 kΩ at 25.0 °C respectively. A magnetic stirrer of submarine type (M-3, Iuchi

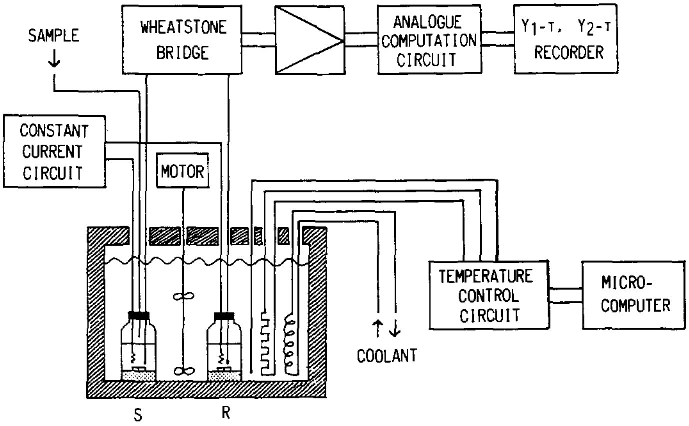

Fig. 1. Schematic diagram of the heat exchange calorimeter.

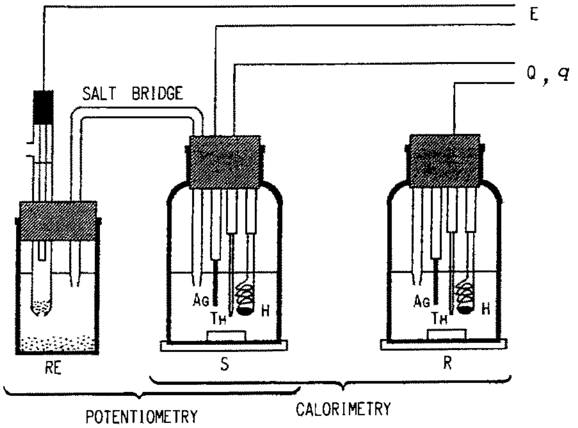

Fig. 2. Detail of sample and reference vessels: S, sample; R, reference; RE, reference electrode; H, heater element; Th, thermistor; Ag, silver rod used as the electrode.

Seieido Co., Tokyo) was used for effective agitation of each vessel. The heat evolution from the stirrer motors and from the motor-driven stirrer was considered as part of the heater power in the temperature-control system [14]. The observed temperature signals, E_0, which are proportional to the observed temperature θ, were converted to E_1 and E_2, which correspond to Q and q respectively, using the analogue computation circuit shown in Fig. 3. Outputs of E_2 and E_1 vs. time t were recorded as q and Q respectively, with a Y_1–t and Y_2–t recorder (R-01, Rika Denki Co., Tokyo).

The potentiometric cell was constructed in the usual manner, as shown in Fig. 2. The potential difference E of bromide ions against the reference electrode shown in Fig. 2 as RE, composed of a commercially available saturated Ag–AgCl electrode, a saturated potassium chloride solution and a salt bridge, was monitored with a digital voltmeter (SC-31, Thinky, Tokyo) and a Y–t recorder.

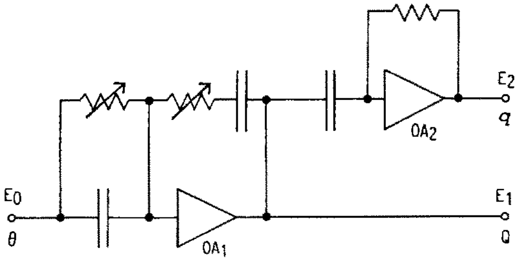

Fig. 3. Analogue computation circuit: OA_1 and OA_2, operational amplifiers.

Procedure

Aliquots of 50.0 g of the mixture of potassium bromate, sulphuric acid and malonic acid were weighed out and placed in the sample and reference vessels. To maintain a good reproducibility, it is not recommended that the mixtures be measured by volume. The vessels were placed in the water bath. The temperature-control system for the bath water, monitored by an 8-bit microcomputer (M5, SORD Co., Tokyo), was then turned on. After a lapse of 40 or 50 min, temperature equilibrium in the water bath was attained and most of the electrical instruments, including the Wheatstone bridge, were warmed up. The off-set voltages of the operational amplifiers in the analogue circuit were adjusted carefully to obtain an output small enough to record a horizontal baseline. Then, from the time lapse of the traces, recorded as Q from the output of the analogue computation circuit, the time constants of the circuit were fitted to the corresponding constants of the calorimeter by adjusting the variable resistors of the circuit. Joule heats were measured. The oscillation reaction was initiated by adding directly the cerium(IV) salt to the solution in the sample vessel from the outside of the calorimeter. The time necessary for dissolving the solid had a negligible influence on the induction period, as it was powdered to accelerate dissolution.

RESULTS AND DISCUSSION

In calorimetric investigations of B–Z reactions, the use of heat exchange calorimetry, in which the temperature of the water bath is controlled precisely [14], is necessary in order to carry out reproducible experiments at constant temperature. While considerable heat is released in the induction period, as discussed later, it is exchanged at once with the ambient water so that the reaction rates of B–Z reactions are not affected by the heat evolved. Accurate estimations of q depend entirely on the stability of the temperature of the bath water, owing to the differentiation factor of q.

The practical influence of immersing the electrode and the salt bridge on the calorimetric estimations was examined in the heat range from 8 to 20 J. The heat calibration value estimated as Joule heat was 0.3917 ± 0.0013 J mm^{-1} in normal calorimetry; when the electrode was installed in the S vessel only, the corresponding value was 0.3989 ± 0.0010 J mm^{-1}. However, with the set-up described above, the equipment compensated well for the thermal effect in both the S and R vessels, the heat calibration value being 0.3910 ± 0.0010 J mm^{-1}. The effect of the salt bridge composed of nitrate and agar on the calorimetry and the oscillation is negligibly small and its use in acid solutions introduces no complications.

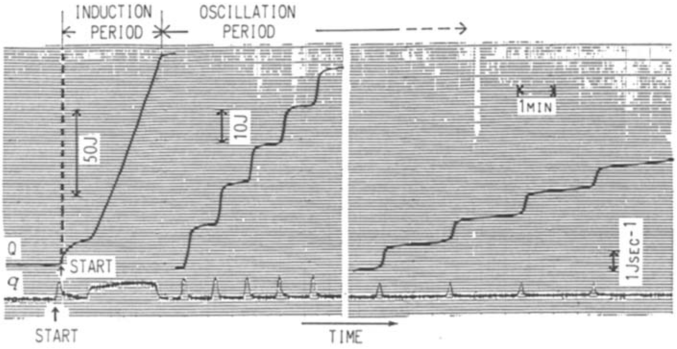

Fig. 4. Typical calorimetric curves for the B–Z reaction in the solution composed of $KBrO_3$ (0.0700 M), H_2SO_4 (0.500 M), $CH_2(COOH)_2$ (0.300 M) and Ce(IV) salt (2.13×10^{-3} M): *q*, rate of heat evolution; *Q*, total heat effect.

The induction period of the chemical oscillations does not appear in experiments in a continuous-flow stirred tank reactor [3]. However, in the case of the batch-type apparatus reported here, it does appear and its duration depends on the concentration of the constituent materials [15]. Typical *Q* and *q* traces are shown in Fig. 4. Just after the addition of cerium(IV) salt initiator, a total heat evolution of $122.4 \pm 0.0_5$ J, a mean of five runs, was observed in 50.0 g of the mixture of malonic acid (0.300 M), potassium bromate (0.0700 M), sulphuric acid (0.500 M) and cerium(IV) salt (2.13×10^{-3} M), these concentrations having been selected from preliminary experiments as a typical mixture; in contrast, only a small change in potential difference *E* was observed, as shown in Fig. 5. The term induction period was used to describe the reaction from the beginning to the end of the large heat evolution; an oscillation period then followed. Ammonium cerium(IV) nitrate was also used as the catalyst; no essential difference from the sulphate was found. The reproducibility of *Q* in each oscillation was about 1–3% in several runs under almost the same experimental conditions. In this report, two periods are discussed separately.

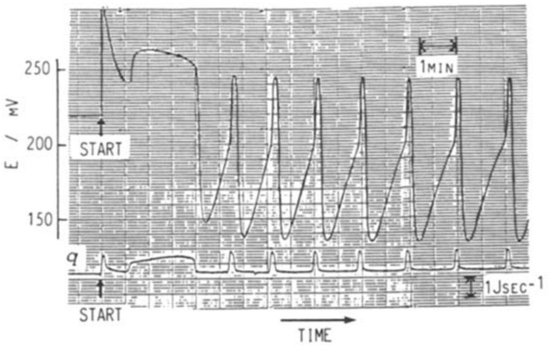

Fig. 5. Typical potentiometric and calorimetric curves in the same solution as in Fig. 4: *q*, rate of heat evolution; *E*, potential difference of [Br^-] vs. the reference electrode.

A simplified oscillation scheme of the B–Z reactions is proposed in the following expressions [2].

Process A:

$$Br^- + HBrO + H^+ \rightarrow Br_2 + H_2O \quad (1)$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2HBrO \quad (2)$$

$$Br^- + BrO_3^- + 2H^+ \rightarrow HBrO + HBrO_2 \quad (3)$$

Process B:

$$2HBrO_2 \rightarrow BrO_3^- + HBrO + H^+ \quad (4)$$

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\bullet + H_2O \quad (5)$$

$$BrO_2\bullet + Ce(III) + H^+ \rightarrow HBrO_2 + Ce(IV) \quad (6)$$

Process C:

$$CH_2(COOH)_2 + 2HBrO \rightarrow BrCH(COOH)_2 + 2H_2O \quad (7)$$

$$4Ce(IV) + BrCH(COOH)_2 + H_2O$$
$$\rightarrow 4Ce(III) + HCOOH + 2CO_2 + Br^- + 5H^+ \quad (8)$$

The reactions were repeated in the order A, B, C. When the malonic acid was consumed and decreased to the threshold concentration, the oscillation ceased. The concentration of bromide ions may reflect the reaction process. To describe the reaction mechanism, these expressions are also used below.

Induction period

The total heat effect released in the induction period, Q_{ind}, depends on the initial concentration of each component. The observed Q_{ind} increased linearly with increase in sulphuric acid concentration from zero to 0. 900 M in several runs carried out in solutions also containing 0.300 M malonic acid, 0.0700 M $KBrO_3$ and 2.13×10^{-3} M $Ce(NH_4)_4(SO_4)_4$. The same linear relation was obtained with an increase in $KBrO_3$ concentration from zero to 0.0700 M. While a linear relation between Q_{ind} and the initial concentration of malonic acid was also observed in the range 0.0500–0.500 M, the variation in cerium(IV) concentration did not produce the same effect on Q_{ind}. Therefore the concentration range of each component was not necessarily critical.

Plots of the induction time (s) vs. initial concentration of sulphuric acid, $[H_2SO_4]_{init}$, are shown in Fig. 6A. The plateau region of the plots begins at 0.5 M $[H_2SO_4]_{init}$, which is consistent with the concentration of sulphuric acid selected from potentiometry as a typical concentration. The equivalent plots for $[KBrO_3]_{init}$ are shown in Fig. 6B; they are also consistent with those reported [15].

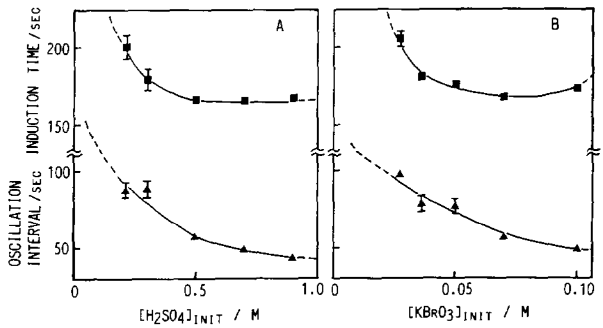

Fig. 6. Induction time and mean oscillation interval 10 min from the start: A, $[H_2SO_4]_{init}$; B, $[KBrO_3]_{init}$.

Details of Q_{ind} were observed in separate runs under the same experimental conditions, as shown in Table 1, in which the observed results are adjusted to the typical concentrations of the components. The values of Q_6–Q_{10} were estimated arithmetically.

TABLE 1

Calorimetric estimations in the induction period of the B–Z reaction

Notation	Estimated heat [a] (J)	Process
Q_1	1840 [b]	Dilution of H_2SO_4 solution
Q_2	$-290.7 \pm 1.1_5$	Dissolution of $CH_2(COOH)_2$(s) in water
Q_3	$-137.4 \pm 0.1_6$	Dissolution of $KBrO_3$(s) in water
Q_4	$-1.14 \pm 0.01_2$	Dissolution of $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$(s) in water
$Q_3 + Q_6 + Q_8$	$-133.5 \pm 0.1_9$	Dissolution of $KBrO_3$(s) in solution of $CH_2(COOH)_2$ and H_2SO_4
$Q_3 + Q_6 + Q_{10}$	$-135.3 \pm 0.1_4$	Dissolution of $KBrO_3$(s) in solution of Ce(IV) salt and H_2SO_4
$Q_3 + Q_{10}$	$-137.6 \pm 0.06_7$	Dissolution of $KBrO_3$(s) in Ce(IV) salt solution
$Q_4 + Q_7 + Q_9$	$12.0 \pm 0.1_0$	Dissolution of Ce(IV) salt(s) in solution of $CH_2(COOH)_2$ and H_2SO_4
$Q_4 + Q_9 + Q_{10}$	$15.9 \pm 0.02_2$	Dissolution of Ce(IV) salt(s) in solution of $CH_2(COOH)_2$ and $KBrO_3$
Q_6	2.35	Heat of reaction of H_2SO_4 with $KBrO_3$
Q_7	-4.09	Heat of reaction of H_2SO_4 with Ce(IV) salt
Q_8	1.05	Heat of reaction of $CH_2(COOH)_2$ with $KBrO_3$
Q_9	17.19	Heat of reaction of $CH_2(COOH)_2$ with Ce(IV) salt
Q_{10}	-0.17	Heat of reaction of Ce(IV) salt with $KBrO_3$

[a] Endothermic heat indicated with a minus sign.

[b] Calculated from literature values [17].

In the induction period evolution of the heat apparently takes place in two steps. The first step is the evolution of the heat of dissolution of cerium (IV) salt in the solution in the sample vessel. When powdered $KBrO_3$ was used as the starter, a large endothermic heat change was observed in the first step. The second step is believed to be the evolution of the heat of reaction of malonic acid with cerium(IV) salt (Process C) which corresponds to reduction of cerium(IV) to cerium(III), and to the colour change of the solution from yellow to colourless. The net heat evolved in the induction period in the solution was estimated to be $110.6 \pm 0.9_3$ J. Even if sulphuric acid and $KBrO_3$ were not included, positive heat evolution was observed (Table 1). The calorimetric results presented here may not be sufficient for a detailed discussion of the heat evolution mechanism.

Oscillation period

In the oscillation period, the total heat effect released in each oscillation cycle, Q_{osc}, was plotted against the time lapse from the start, t, with varying initial concentrations of the four components. The Q_{osc} value decreased with decrease in the initial concentration. An exponential decrease in Q_{osc} was observed with decreasing H_2SO_4, $KBrO_3$ and cerium(IV) salt concentrations. However, in the case of malonic acid, Q_{osc} decreased with increase in the initial concentration and an irregular curve was observed. The interval of every cycle increased with t. Also the duration of the oscillation decreased with a decrease in the initial concentration. Plots of Q_{osc} vs. t fitted well with the exponential expression, $Q_{osc} = A \exp(Bt) + C$, rather than with $Q_{osc} = At^2 + Bt + C$. The curves obtained for H_2SO_4 are shown in Fig. 7 as an example. The constants A, B and C in the exponential expression were calculated by the method of least squares. For the regions numbered (1)–(8)

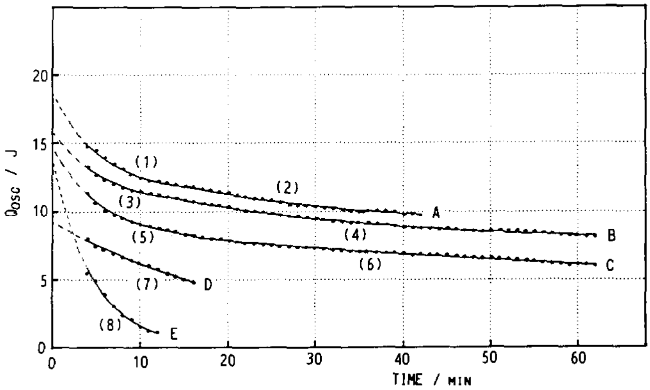

Fig. 7. Q_{osc} evolved at each oscillation cycle with change in $[H_2SO_4]_{init}$: curve A, 0.900 M; curve B, 0.700 M; curve C, 0.500 M; curve D, 0.300 M; curve E, 0.225 M.

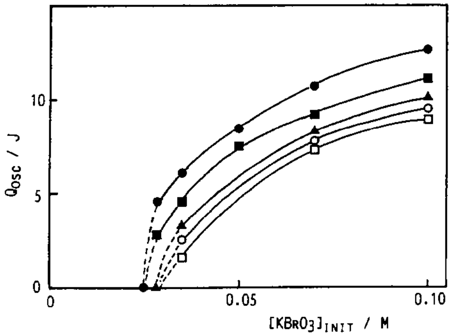

Fig. 8. Plots of Q_{osc} evolved at every oscillation cycle vs. $[KBrO_3]_{init}$: ●, 5 min; ■, 10 min; ▲, 15 min; ○, 20 min; □, 30 min.

in Fig. 7, they were calculated to be (7.310, −0.1818, 11.345), (6.025, −0.0501, 9.057), (5.333, −0.1687, 10.473), (5.696, −0.0392, 7.698), (6.829, −0.1737, 7.860), (5.237, −0.0143, 3.917), (9.185, −0.0394, 0) and (13.715, −0.2137, 0) respectively. Almost the same plots were obtained for the other components and the constants were also calculated. Plots of Q_{osc} vs. $[KBrO_3]_{init}$ were obtained at 5 or 10 min intervals from the start, (see Fig. 8). The zero of Q_{osc} at about 0.0250 M $[KBrO_3]_{init}$ was considered to be the threshold concentration for starting the oscillation. The critical concentration was observed to be 0.150 M in H_2SO_4. If any oscillation occurred, heat evolution was observed.

The effect of the initial concentration of each component on q, as well as on Q and E, was studied. Typical q results obtained in Ce(IV) salt are shown in Fig. 9. As the concentration of Ce(IV) salt decreased from 4.00×10^{-3} to 0. 600×10^{-3} M, the peak height of q became lower and the

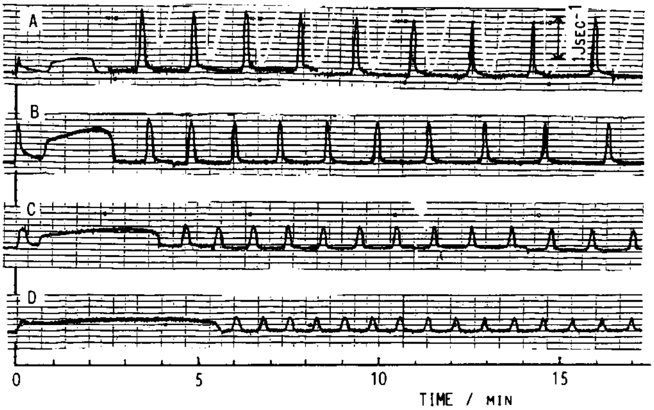

Fig. 9. Influence of the variation of [Ce(IV) salt]$_{init}$ on the observed q against t: A, 4.00×10^{-3} M; B, 2.13×10^{-3} M; C, 0.999×10^{-3} M; D, 0.600×10^{-3} M.

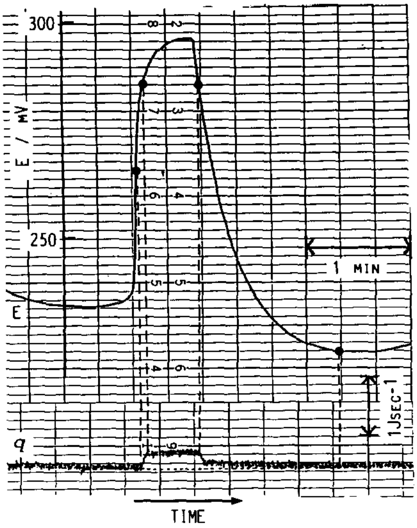

Fig. 10. One cycle of oscillation of q and E measured in the solution composed of $CH_2(COOH)_2$ (0.0600 M), $KBrO_3$ (0.0700 M), H_2SO_4 (0.500 M) and Ce(IV) salt (2.13×10^{-3} M).

oscillation intervals decreased. At the same time, the duration of the induction periods became longer and the magnitudes of q became smaller and broader. In Fig. 9A, Q_{ind} was recorded in reduction by a factor of 0.3. In the cases of H_2SO_4 and $KBrO_3$, almost the same curves of q against t were obtained as those in cerium(IV) salt, but the induction periods did not change with the initial concentration. With a decrease in the concentration of malonic acid, the peak width of q increased. The characteristic oscillations in q were obtained in the minimum concentration of 0.0600 M and the oscillation curve of E vs. t was different from that of the others. Figure 10 shows one cycle of two typical E vs. t and q vs. t curves, which were recorded on a two-pen recorder; for clarity, one curve was shifted to cancel the discrepancy between the two pens. Specific points in q are related to the upper curve of E by broken lines. One cycle of q and E vs. t is shown in Fig. 11 which was recorded in typical concentrations of the components, as in Fig. 10. In Fig. 11, the numbers 1–3 on the E(mV) curve correspond to the start, maximum and end points of the heat evolution rate in the q vs. t curve respectively. The threshold or critical concentration of bromide ions from Process A to Process B was given by $(k5/k2)[BrO_3^-]$, where $k2$ and $k5$ are the rate constants of reactions (2) and (5) respectively. The threshold concentration of bromide ions, $[Br^-]_{\text{crit}}$, was calculated to be 5×10^{-6} $[BrO_3^-]$ and 1.4×10^{-5} $[BrO_3^-]$ from the literature values of the rate constants [2,18], and indicated as 0.35×10^{-6} M for ref. 2 and 0.98×10^{-6} M for ref. 18 (see the dotted lines on Fig. 11). The decrease in bromide ions (from points 1 to 2 in Fig. 11) corresponds to the transfer from Process A to

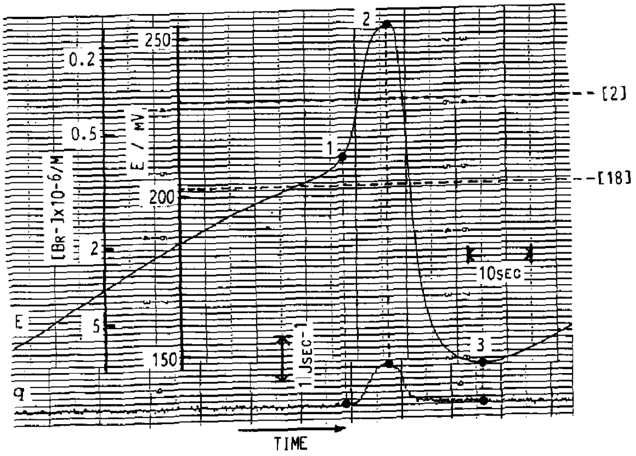

Fig. 11. One cycle of oscillation of q and E in a solution of the same constitution as that used in Figs. 4 and 5. The broken lines refer to the literature values.

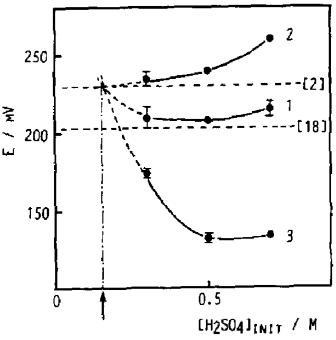

Fig. 12. Plots of E vs. $[H_2SO_4]_{init}$. The numbers 1–3 correspond to those in Fig. 11.

Process B, and their increase (from points 2 to 3) corresponds to Process C. Therefore the heat evolution may correspond to Process B and Process C. Almost the same result was found in Fig. 10; the plateau in the q values was characteristic. The processes indicated are believed to overlap with each other, from the presence of an obvious tail on the right-hand side of the peaks of q. The potential differences at points 1, 2 and 3 were observed when $[H_2SO_4]_{init}$ was varied and are plotted in Fig. 12 . The extrapolated curves meet at a point on the broken lines calculated from ref. 2, of which $[H_2SO_4]_{init}$ was 0.150 M as indicated by the arrow, corresponding to a point at which Q_{osc} was zero in plots of Q_{osc} vs. $[H_2SO_4]_{init}$.

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