Temperature Oscillations in Bromate–Gallic Acid System: A Calorimetric Study

KALLOL MUKHERJEE and S. P. MOULIK
Center for Surface Science, Department of Chemistry, Jadavpur University, Calcutta, 700 032, India

D. C. MUKHERJEE
Department of Pure Chemistry, Calcutta University, Calcutta, 700 009, India

Abstract

The oscillatory reaction between potassium bromate and gallic acid in sulfuric acid medium has been studied calorimetrically with and without ferroin indicator. Enthalpy changes during oscillations have increased with increasing bromate concentration in presence and absence of the indicator. Prominent catalytic activity of the indicator has been observed. An initial large enthalpy change has been observed in both uncatalyzed and catalyzed conditions prior to the starting of oscillation. Attempts have been made to correlate the main thermal events with the proposed mechanism of the reaction. © 1995 John Wiley & Sons, Inc.

Introduction

In Belousov-Zhabotinsky (B-Z) oscillatory reactions two chemical forms (usually oxidized and reduced forms) interchange in definite time intervals and the process continues for some time depending on environmental conditions. The mechanism of B-Z reaction has been given by Noyes et al. [1] and subsequently detailed studies have been made by others [2–20]. The reaction has been also studied in aquo-organic solvent media [21]. The physical methods normally used to study such reactions are spectrophotometry [3,4], potentiometry [5], and thermometry [5,6,8,10], and the malonic acid/sulfuric acid catalyzed by cerium ion system has been the one mostly studied [5–9,15–19]. Catalysis of this system by ferroin has been investigated and quantitative mathematical models have been proposed [16,17]. Oxidation kinetics of ferroin-bromate system and bromomalonic acid–ferriin system have been also studied [18,19]. The gallic acid/bromate/sulfuric acid system has been relatively less explored [10–14]. The temperature oscillations of this system has been reported by Koros et al. [10] but thermodynamic analysis of this and other oscillatory systems have been rarely made. Apart from documentation values, the energetic informations on the process may give insight to the mechanism of the oscillatory reactive process. A sensitive calorimeter can serve the purpose. Since the thermometric method has been much less explored [6,8,10], we have attempted to use the method in the overall and detailed understanding of the oscillatory reaction of gallic acid/bromate/sulfuric acid system in the absence and presence of ferroin indicator in a Tronac-458 isoperibol calorimeter. Quantification of the reactive process has been attempted.

International Journal of Chemical Kinetics, Vol. 27, 561–568 (1995)

CCC 0538-8066/95/060561-08

Experimental

Materials

Potassium bromate, sulfuric acid, and gallic acid used were of E. Merck, Germany. Ferroin indicator was prepared in the usual way [13]. The surfactant cetyltrimethyl ammonium sulfate (CTAS) used was prepared from its bromide (CTAB), a Sigma product by ion exchange method.

Method

The reaction was studied in a TRONAC-458 isoperibol calorimeter at 30°C. 0.015 gm gallic acid was dissolved in 19 ml. of 3.6 equiv. dm^{-3} H_2SO_4 with one drop of ferroin in the reaction vessel of the calorimeter. A freshly prepared solution of potassium bromate in 3.6 equiv. dm^{-3} H_2SO_4 was added from the burette for 2–4 min in different runs to obtain different bromate concentrations. Several runs were also carried out without the ferroin indicator. The heat change during the oscillations was recorded with a Houston Omniscribe Stripchart Recorder. The heat produced during the oscillation was evaluated following the procedure described earlier [22,23].

The cmc of the surfactant (CTAS) was determined in 3.6 equiv. dm^{-3} H_2SO_4 medium by surface tension method in a Kruss (du-Nuoy) Tensiometer, Germany in the usual way [22]. It was found to be 0.013 m mol dm^{-3} in 3.6 equiv. dm^{-3} of H_2SO_4 at 303 K.

Results and Discussion

Oscillations and the Associated Heat

The addition of bromate in the gallic acid/sulfuric acid mixture resulted both release and absorption of heat in stages. A large exothermic stage was observed just after the start of the addition of bromate which continued for a period of one and half minutes. It was not contaminated with the oscillatory process which started well after the addition of bromate was complete. The analysis of the thermometric results was therefore distinct and straight forward. Thereafter, the process was to some extent endothermic. After the total addition of bromate, a moderate amount of heat was further released which was followed by release of a large amount of heat within a short time interval. The exothermic event then appeared periodically with lesser degree of intensity and disappeared after several cycles. This was the oscillatory part of the reaction process. The initial release of heat followed by the oscillatory heats (manifested as fluctuation of temperature) are depicted in Figure 1. The initial heat corresponds to an enthalpy (ΔH) of −2.6 kJ mol^{-1} of bromate. The oscillatory thermograms are systematic and well formed. The number of oscillations was greater in presence of the catalyst ferroin than in its absence. The number also decreased with decreasing $[BrO_3^-]$. In Figure 2, the profiles of the appearance of successive oscillations at different times for different $[BrO_3^-]$ in presence of the catalyst are presented. The total number of oscillations as a function of $[BrO_3^-]$ is depicted in Figure 3. The ferroin catalyzed situation was much more efficient at $[BrO_3^-] > 0.015$ mol dm^{-3}. At $[BrO_3^-] < 0.007$ mol dm^{-3}, hardly any oscillation occurred in 1000 s which became eight at $[BrO_3^-] = 0.020$ mol dm^{-3}. The number was only three at this concentration of bromate in the absence of catalyst.

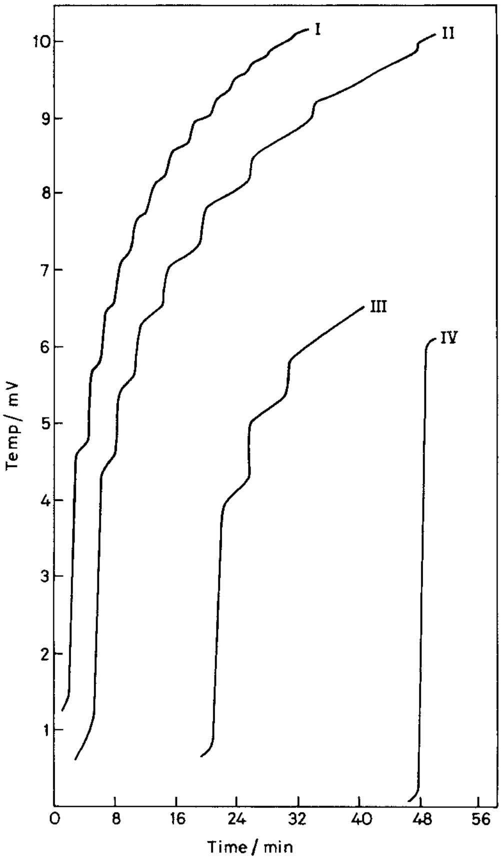


Figure 1. Thermograms of oscillations of the reaction bromate/gallic acid/sulfuric acid at [gallic acid] = 4.4 m mol dm^{-3} at 303 K. (I) and (II): With [ferroin] = 4 × 10^{-5} mol dm^{-3}; [BrO_3^-] = 0.019 mol dm^{-3} (I); and [BrO_3^-] = 0.017 mol dm^{-3} (II). (III): Without ferroin at [BrO_3^-] = 0.019 mol dm^{-3}. (IV): Initial release of heat due to addition of bromate to gallic acid.

Enthalpy of Oscillation

The enthalpies for successive oscillations at different times are illustrated in Figure 4. The open and closed points correspond to catalyzed and uncatalyzed runs. It was observed that the enthalpies of the successive oscillations in presence and absence of ferroin were more or less the same and were independent of [BrO_3^-]. The nature of the courses was also on the whole identical. The profiles of total enthalpy (ΔH_T) of the oscillatory process depicted in Figure 5 as a function of [BrO_3^-] evidence more release of heat in presence of ferroin at all [BrO_3^-]. Like the total number of oscillations, ΔH_T also has a tendency of sharp increase at [BrO_3^-] > 0.017 mol dm^{-3}. In the uncatalyzed condition, ΔH_T has a levelling off tendency at [BrO_3^-] > 0.015 mol dm^{-3}. The catalyst thus increased the frequency by shortening the time interval. The quick oscillations in presence of ferroin were delayed in its absence. The ferroin catalyst essentially increased the number of oscillations [11]. In absence of the external catalyst, the oscillations were largely damped. A representation of the enthalpies of the oscillatory steps (expressed per unit duration time) with respect to time elapsed at different [BrO_3^-] in presence of catalyst is presented in Figure 6.

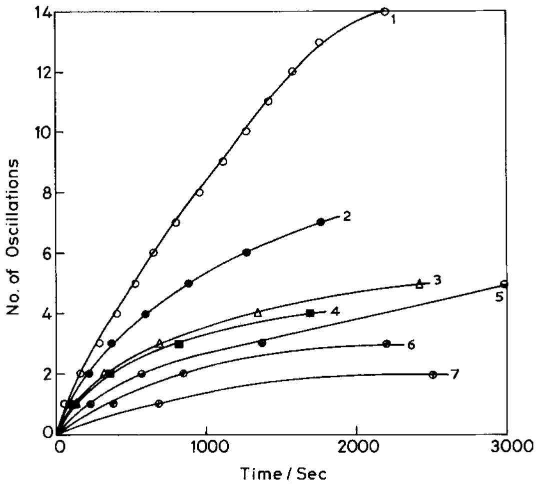


Figure 2. Plot of number of oscillations vs. time for gallic acid-bromate reaction at 4.4 m mol dm^{-3} gallic acid and 4 × 10^{-5} mol dm^{-3} ferroin at 303 K. Curves (1 → 7): [BrO_3^-] = 0.019, 0.017, 0.016, 0.015, 0.0135, 0.011, and 0.01 mol dm^{-3}.

The nice stepwise and systematic decline of enthalpy with time is evident. The initial large negative enthalpy (exothermicity) followed by a mild endothermic nature of the thermochemical event of gallic acid/bromate/sulfuric acid system in the presence and absence of catalyst prior to oscillation was not reported in the past. Its magnitude was found to be independent of the experimental conditions. This first large enthalpy change is considered to be related to the oxidation of the gallic acid which is one of the vital steps for the oscillatory process. After the addition of bromate, in the first step, gallic acid is oxidized to its quino-noid from Q that acts as an effective catalyst in the oscillatory process in the absence of external catalyst [13].

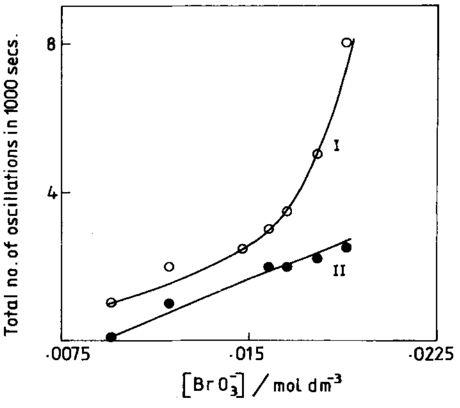


Figure 3. Variation of oscillation number per 1000 s with [BrO_3^-] at 4.4 m mol dm^{-3} gallic acid at 303 K. (I): [Ferroin] = 4 × 10^{-5} mol dm^{-3}. (II): Without ferroin.

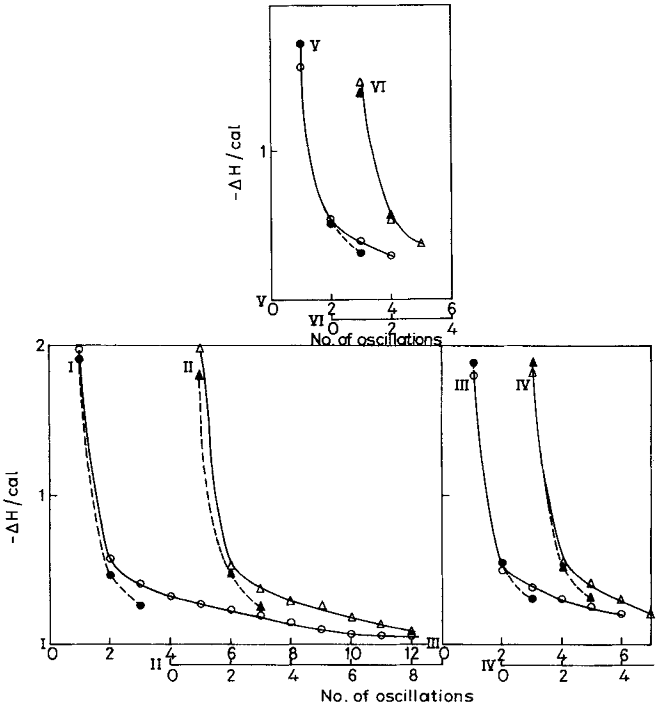


Figure 4. Enthalpy change per oscillation vs. oscillation number profile at 303 K and 4.4 m mol dm^{-3} gallic acid. Curves (I–VI): $[BrO_3^-] = 0.019, 0.017, 0.016, 0.015, 0.0135$, 0.011, and 0.01 mol dm^{-3}. (Open points): [Ferroin] = 4×10^{-5} mol dm^{-3}. (Closed points): Without ferroin.

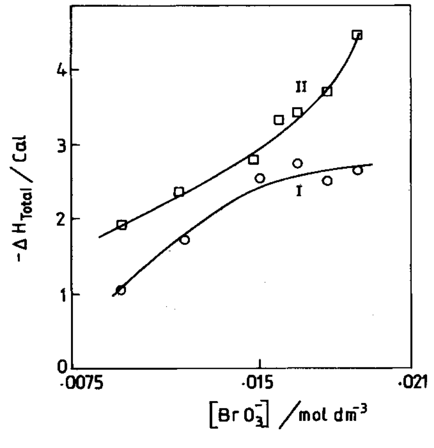


Figure 5. Total heat change in the reaction as a function of $[BrO_3^-]$ at 303 K and at 4.4×10^{-3} mol dm^{-3} gallic acid. (I): Without ferroin. (II): [Ferroin] = 4×10^{-5} mol dm^{-3}.

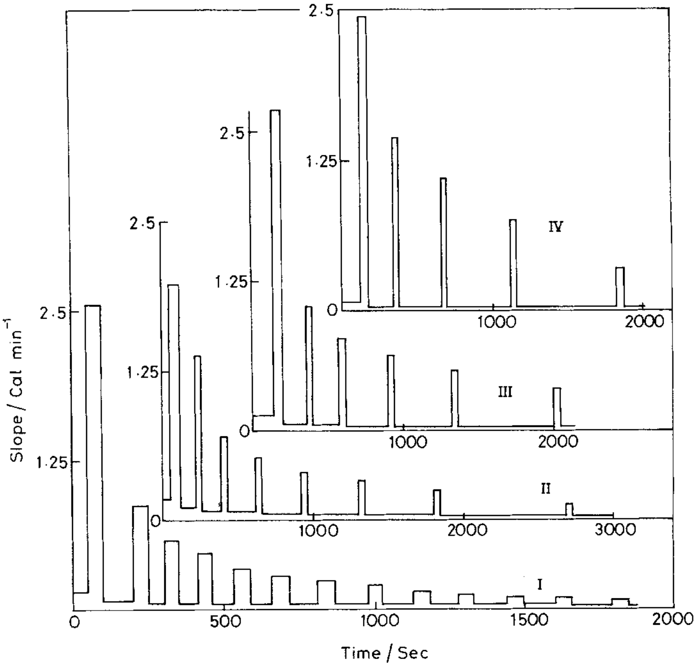
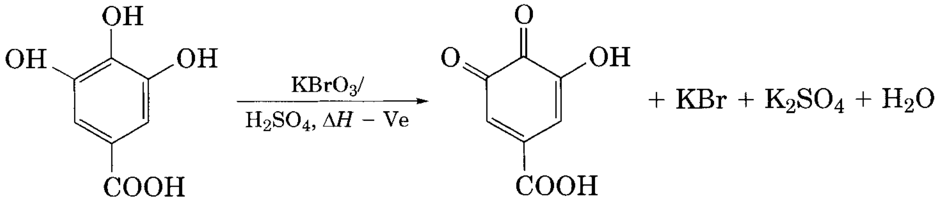
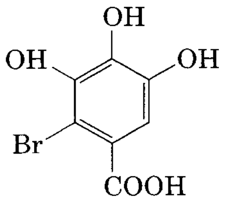


Figure 6. The rate of heat change for the thermal oscillation as a function of time. [Gallic acid] = 4.4 × 10^{-3} mol dm^{-3}: [Ferroin] = 4 × 10^{-5} mol dm^{-3}. (I–IV): [BrO_3^-] = 0.019, 0.017, 0.016, and 0.015 mol dm^{-3}.

(I)



Then, reacting with the bromine radical $(\mathrm{B}\dot{\mathrm{r}})$, Q undergoes bromination and subsequent formation of bromogallic acid



These steps are followed by oscillatory events

There, either

(II) $$BrO_3^- + 2Q + H^+ \xrightarrow[\text{Uncatalyzed}]{} HBrO_2 + 2\dot{Q} + H_2O$$

or

(III) $$BrO_3^- + 2Fe^{2+} + 3H^+ \xrightarrow[\text{Catalyzed}]{} HBrO_2 + 2Fe^{3+} + H_2O$$

also produces negative enthalpy to a lesser degree. The red color of the indicator changes to green during this process for the catalyzed system. The above reactions are in accordance with the propositions made by Field et al. [5] and Liu et al. [13]. During the reversal of the above forward process we are in favor of considering reactions IV and V in the uncatalyzed and catalyzed conditions, respectively.

(IV) $$2\dot{Q} + BrGA + H_2O \xrightarrow[\text{Uncatalyzed}]{} Br^- + 2Q + \text{Ketonic acid} + H^+$$

and

(V) $$4Fe^{3+} + BrGA + H_2O \xrightarrow[\text{Catalyzed}]{} Br^- + 4Fe^{2+} + \text{Ketonic acid} + 5H^+$$

The color changes from green to red during the process (V) in the catalyzed system. The step (IV) or (V) is associated with the negligibly small enthalpy change (supported by the observed thermal event of the reaction) and terminates the production of $HBrO_2$ and initiates the repeat of a cycle.

Zhabotinsky et al. [16] suggested that in the ferroin catalyzed B-Z reaction, the catalyst remained almost completely oxidized during a significant part of the oscillatory cycle. The suggested mathematical model indicated reversibility of the catalyst oxidation by bromine dioxide radical. A similar step may also contribute in the mechanistic course of the present GA-bromate–ferroin oscillatory reaction.

The distinct color changes in a cycle were visually monitored performing identical experimental runs outside the calorimeter. For our thermochemical interest, the events were not spectrophotometrically probed. However, the uncatalyzed runs herein studied could not be probed by spectral means.

The *i*th oscillations in the presence and absence of ferroin indicator (envisaged in eq. (II) and (III) are associated with more or less equal magnitudes of ΔH. The number of oscillations, *n*, however, is much less in the absence of ferroin. It appears that there is a threshold barrier that must be reached and the added ferroin indicator helps the system to quickly attain this. The Q is much weaker than Fe^{2+} in this respect. This phenomenon is comparable with the impulse generation during nerve conduction which obeys "all or none rule" [24]. Once this threshold is reached, the oscillation starts with associated release of heat independent of both Fe^{2+} and Q.

Micellar Effect

The micellar environment of CTAS minorly affects the thermochemical property of the reaction. The oscillations increased only by a small number. At [CTAS] = 0.15, 0.3, 0.45, and 0.75 m mol dm^{-3}, the respective numbers of oscillations (in 1000 s) were found to be 11, 9, 12, and 10. Without CTAS, the number of oscillations were eight.

Conclusion

The reaction between bromate, gallic acid, and sulfuric acid shows temperature oscillations both in presence and absence of ferroin. The number of oscillations as well as total enthalpy change of the reaction depends on bromate concentration and show a nonlinear dependence with $[BrO_3^-]$, they are also different for the catalyzed and uncatalyzed conditions. Although the time consumed between two successive oscillations is more without the catalyst, the enthalpy changes for the successive oscillations are independent of $[BrO_3^-]$ as well as the indicator catalyst ferroin. The enthalpy change per oscillation in the reaction decreases assymptotically with time.

Acknowledgment

This work was financially supported by a CSIR Senior Research Fellowship to K. M. We thank Dr. R. S. Banerjee of the Department of Pure Chemistry, Calcutta University for his valuable suggestions. We are obliged to the reviewer who has called our attention to refs. [16–19].

Bibliography

[1] R. M. Noyes and R. J. Field, *Ann. Rev. of Phys. Chem.,* **25,** 95 (1974).
[2] R. M. Noyes, *J. Am. Chem. Soc.,* **102,** 4655 (1980).
[3] P. G. Bowers, K. E. Caldwell and D. F. Prendergast, *J. Phys. Chem.,* **76,** 2185 (1972).
[4] G. J. Kasperek, and T. C. Bruice, *Inorg. Chem.,* **10,** 382 (1971).
[5] R. J. Field, E. Koros, and R. M. Noyes, *J. Am. Chem. Soc.,* **94,** 8649 (1972).
[6] (a) E. Koros, M. Orban, and Z. Nagy, *Nature, Phys. Sci.,* **233** 137 (1971), **242,** 30 (1973), (b) *J. Phys. Chem.,* **77,** 3122 (1973).
[7] R. P. Rastogi, K.D.S. Yadava, and A. Kumar, *Ind. J. Chem.,* **12,** 1282 (1974).
[8] H. G. Busse, *J. Phys. Chem.,* **73,** 750 (1969).
[9] R. P. Rastogi and K.D.S. Yadava, *Nature,* **240,** 19 (1972).
[10] (a) E. Koros and M. Orban, *Nature,* **273,** 371 (1978); (b) *J. Phys. Chem.,* **82,** 1672 (1978).
[11] (a) J. J. Jwo and E. F. Chang, *J. Phys. Chem.,* **2388,** 93, (1989); (b) *J. Chin. Chem. Soc. (Taipe),* **33,** 93 (1986).
[12] J. S. Babu, K. Srinivasalu, and M. M. Bokadia, *Bull. Chem. Soc. Jpn.,* **49,** 2875 (1976).
[13] J. Liu and S. K. Scott, *J. Chem. Soc. Faraday Trans.,* **87,** 2135 (1991); **88(7),** 909 (1992).
[14] R. M. Noyes, R. J. Field, and E. Koros, *J. Am. Chem. Soc.,* **94,** 1394 (1972).
[15] M. Orban, E. Koros, and R. M. Noyes, *J. Phys. Chem.,* **83,** 3056 (1979).
[16] A. M. Zhabotinsky, F. Bucholtz, A. B. Kiyatkin and I. R. Epstein, *J. Phys. Chem.,* **97,** 7578 (1993).
[17] A. B. Rovinsky and A. M. Zhabotinsky, *J. Phys. Chem.,* **88(25),** 6081 (1984).
[18] A. B. Rovinsky and A. M. Zhabotinsky, *Teor. Eksp. Khim.,* **15(1),** 25 (1979).
[19] A. B. Rovinsky, *J. Phys. Chem.,* **88,** 4 (1984).
[20] *Oscillations and Travelling Waves in Chemical System,* R. J. Field and M. Burger, Eds., Wiley, New York, 1985.
[21] P. V. Lalitha and R. Ramaswamy, *Int. J. Chem. Kinet.,* **25(6),** 457 (1993).
[22] P. K. Jana and S. P. Moulik, *J. Phys. Chem.,* **95,** 9525 (1991).
[23] K. Mukherjee, D. C. Mukherjee, and S. P. Moulik, *Langmuir,* **9,** 1727 (1993).
[24] M. V. Volkenstein, *MIR Moscow,* 1983, p. 381.

Received July 11, 1994
Accepted October 18, 1994