

New uncatalysed bromate-driven oscillators: The Rhodamine B base/ Rhodamine B- BrO_3^- - H_2SO_4 systems

P K SRIVASTAVA* and B N AVASTHI

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

MS received 8 April 1992; revised 21 September 1992

Abstract. New uncatalysed chemical oscillations have been found in the Rhodamine B base- BrO_3^- - H_2SO_4 and Rhodamine B- BrO_3^- - H_2SO_4 systems in a batch reactor. A non-oscillating absorption band due to an intermediate species was isolated, which is anticipated to have close relationship with the one-electron redox couple of these dye oscillators.

Keywords. Uncatalysed oscillation; bromate driven oscillations; Rhodamine B base- BrO_3^- - H_2SO_4 system.

1. Introduction

Uncatalysed chemical oscillations have been reported in a number of phenol and aniline derivatives with bromate in acidic medium (Körös and Orbon 1978) and for a few other organic molecules (Kuhnert and Linde 1977; Faraje and Janjic 1982). Among them, the phenol- BrO_3^- system has been discussed in substantial detail and the main features of uncatalysed oscillation have been explained on the basis of the modified F.K.N. mechanism (Orbon *et al* 1979; Herbine and Field 1980; Rastogi and Srivastava 1987). However, considerable disagreement concerning the reaction scheme appears to persist for the actual systems (Orbon and Körös 1979; Tockstein and Handlirova 1979; Srivastava *et al* 1991). Ramaswamy and Lalitha (1990) have exploited such behaviour for the determination of small concentrations of substances (hydroxy aromatic, aliphatic and inorganic compounds) that react with Br_2 .

In the course of the study of photochemically induced chemical oscillation, we came across Bigelow's (1977) work which reported oscillatory colour fading upon photoirradiation of Rhodamine B. In tracing his results, we found the acidic solution of Rhodamine B or Rhodamine B base to exhibit uncatalysed chemical oscillation on adding BrO_3^- . We present here preliminary results for these bromate-driven oscillators since our findings of the existence of at least two oscillating species and of the existence of an intermediate which can be detected by absorption spectroscopy seem to be important for the establishment of the sequential steps involved in the uncatalysed bromate oscillator. We also believe that this system would be suitable for investigation of the photochemical effect on this type of chemical oscillator.

* For correspondence

2. Experimental

Rhodamine B base (Aldrich), Rhodamine B, NaBrO_3 and H_2SO_4 (Katayama) of analytical grade have been used without further purification. Freshly prepared solutions of Rhodamine B base and Rhodamine B were used. The temperature of the system was maintained at $25 \pm 0.1^\circ\text{C}$ and the solutions were continuously stirred by a magnetic stirrer. The redox potential was monitored by a platinum electrode coupled with a saturated reference calomel electrode. The Br^- potential was monitored by an Ag/AgBr electrode. The indicator electrode was cleaned with 1,2-dichloroethane before each run in order to avoid possible degradation of sensitivity due to surface contamination.

The absorption spectrum was measured using a Hitachi UV.3400 spectrophotometer and a 1 cm optical path-length cubic quartz reactor. The reactor was stirred continuously by a plate type small magnetic stirrer.

3. Results and discussion

A typical result for the Rhodamine B base- BrO_3^- - H_2SO_4 system is shown in figure 1. The redox potential of the acidic solution of the dye increased and its bromide ion potential decreased after addition of the acidic solution of NaBrO_3 , and the initial red-pink colour of the solution turned to yellow due to the formation of Br_2 . The yellow colour was masked by red when the concentration of the dye was higher. After an induction period, the colour changed to brick-red followed by damped potential oscillations. The limit cycle behaviour of the system is shown in figure 2. Measurement of the absorption spectrum of the aqueous solution of Rhodamine B base showed an intense absorption band at 553 nm due to R^+ [Rhodamine B = R] (Sandell and Onishi 1978) and its intensity decreased in the corresponding acidic solution (figure 3a, b). It was also observed that this band disappeared immediately

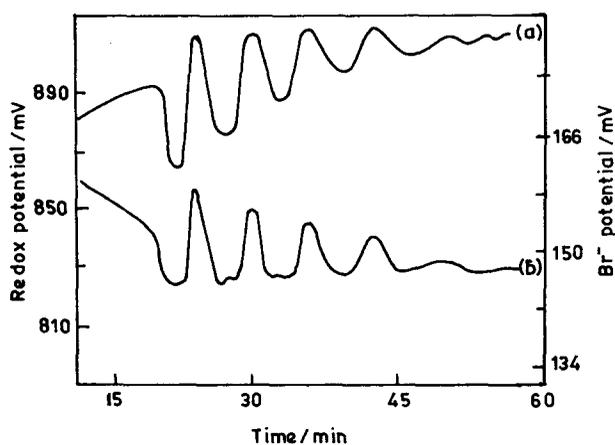


Figure 1. Uncatalysed chemical oscillation for the acidic solution of Rhodamine B base ($3.73 \times 10^{-4}\text{M}$), BrO_3^- ($2.65 \times 10^{-2}\text{M}$) and H_2SO_4 (1.5 M) at $25 \pm 0.1^\circ\text{C}$. The time scale is measured from the time of addition of the BrO_3^- solution (a) Redox potential and (b) Br^- potential.

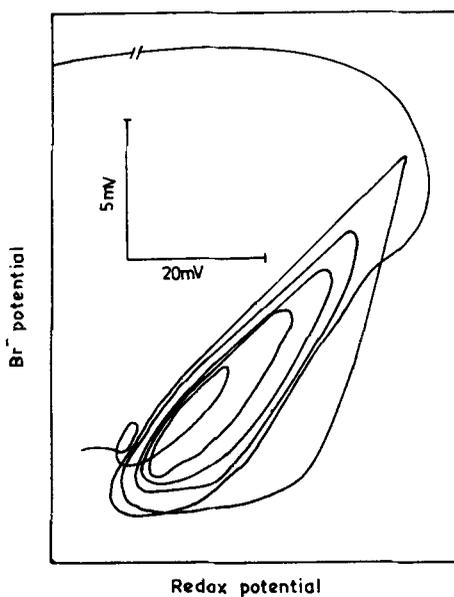


Figure 2. Limit cycle behaviour of Rhodamine B base/ $\text{BrO}_3^-/\text{H}_2\text{SO}_4$ system (compositions same as in figure 1).

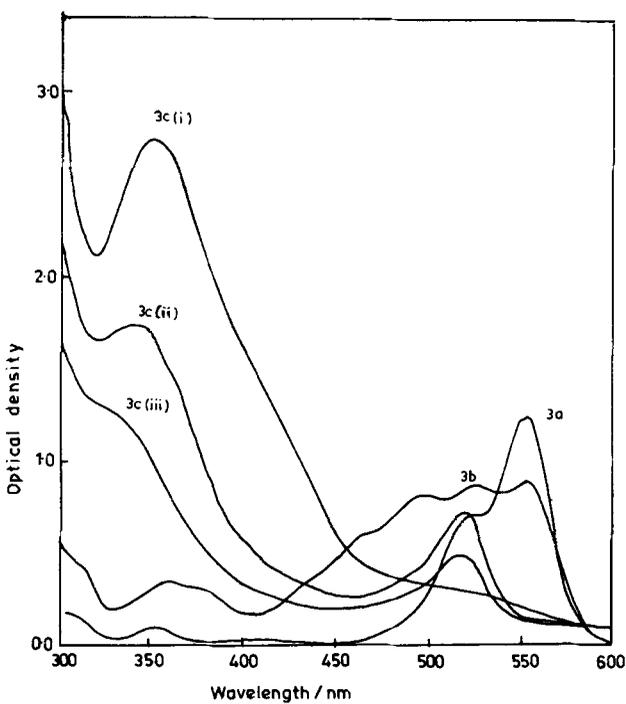


Figure 3. Absorption spectrum (3a) Rhodamine B base ($4.5 \times 10^{-4}\text{M}$) in water, (3b) Rhodamine B Base ($4.5 \times 10^{-4}\text{M}$) in 1.5 M H_2SO_4 , (3c) Oscillatory solution of Rhodamine B base/ $\text{BrO}_3^-/\text{H}_2\text{SO}_4$ system corresponding to compositions as in figure 1 [(i) Immediately after addition of BrO_3^- , (ii) when the oscillation starts and (iii) at the end of oscillation].

after the addition of acidic NaBrO_3 and a new weak band appeared at 518 nm due to the formation of an intermediate. The 518 nm band increased its intensity during the induction period and then decreased (figure 3c [i-iii]) and finally disappeared. Although, this band did not oscillate, its appearance was coincident with the appearance of oscillation of potential. Hence the transient appearance of the intermediate must have close relationship with the instability of the system which causes chemical oscillation. Another absorption band was also observed at 350 nm which may be due to an intermediate. It appeared instantaneously after mixing of BrO_3^- and decreased during the course of reaction.

The oscillation pattern is different for the overall redox potential and the Br^- potential. The redox potential values of figure 1 are comparable to the stationary potential values obtained by Ramaswamy and Lalitha (1990). A comparison of these two patterns indicates that there must be at least one more unknown oscillating species other than Br^- which contributes to the redox potential. The induction time, period of oscillation and number of oscillations were found to be sensitive to the initial concentration and temperature of the constituents. Figure 4 shows the dependence of the induction period with the initial concentration of Rhodamine B base. The range of concentration for which the oscillations were studied are as follows: Rhodamine B base (3.80×10^{-4} – 2.87×10^{-3} M), BrO_3^- (1.13×10^{-2} – 7.95×10^{-2} M)

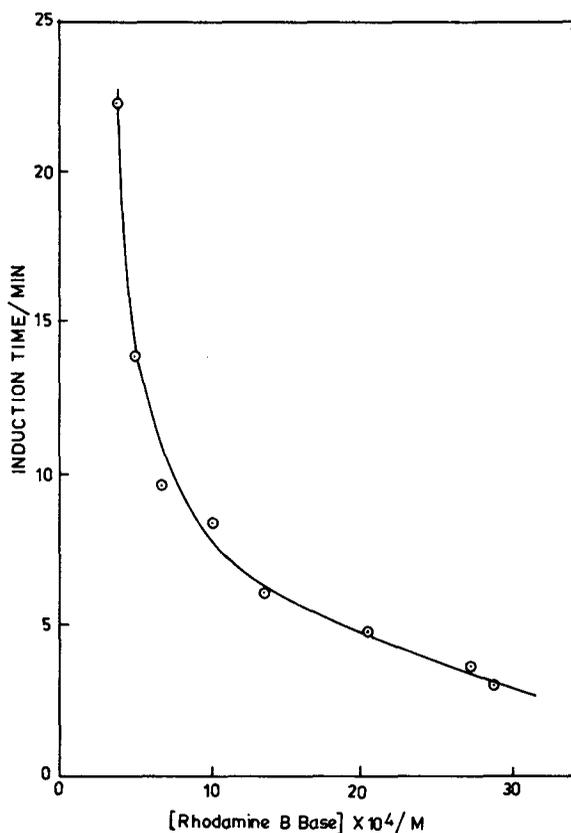


Figure 4. Dependence of induction period on initial concentration of Rhodamine B base.

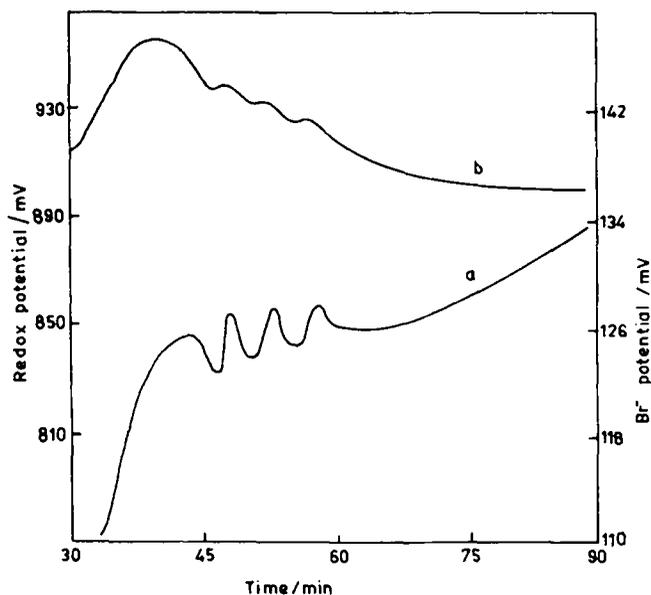


Figure 5. Uncatalysed chemical oscillation for the acidic solution of Rhodamine B ($3.01 \times 10^{-4} \text{ M}$), BrO_3^- ($9.94 \times 10^{-3} \text{ M}$) and H_2SO_4 (1.7 M) at $25 \pm 0.1^\circ\text{C}$. The time scale is measured from the time of addition of the BrO_3^- solution (a) Redox potential (b) Br^- potential.

and H_2SO_4 (0.5–2.3 M), where the higher limit of the dye concentration is limited by its solubility. In determining these ranges, one of the concentrations was changed while the other two were kept at the optimum value: Rhodamine B base ($2.87 \times 10^{-3} \text{ M}$), BrO_3^- ($2.65 \times 10^{-2} \text{ M}$) and H_2SO_4 (1.5 M) at $25 \pm 0.1^\circ\text{C}$. However, for detailed studies the concentration of Rhodamine B base was taken as $3.73 \times 10^{-4} \text{ M}$, as this was found to be most suitable for spectroscopic studies.

Similar behaviour was observed for the Rhodamine B– BrO_3^- – H_2SO_4 system. On adding BrO_3^- to the acidic solution of Rhodamine B, the red colour of the dye changed to yellow due to the formation of Br_2 and then turned to brick-red followed by damped oscillations. The result is shown in figure 5. We have also tried Rhodamine 6G in a similar manner but failed to observe oscillations.

Further investigations are being undertaken in our laboratory to identify the oscillating species and the optically detectable intermediates, as well as study the effect of photoirradiation on the absorption bands of reactants and intermediate species.

References

- Bigelow R W 1977 *J. Phys. Chem.* **81** 88
 Faraje V J and Janjic D 1982 *Chem. Phys. Lett.* **88** 301
 Faraje V J and Janjic D 1982 *Inorg. Chim. Acta.* **65** 2119
 Herbine P and Field R J 1980 *J. Phys. Chem.* **84** 1330
 Körös E and Orbon M 1978 *Nature (London)* **273** 371
 Körös E and Orbon M 1978 *J. Phys. Chem.* **82** 1672

- Kunhert L and Linde H 1977 *Z. Chem.* **17** 19
- Orbon M and Körös E 1979 *Kinetics of physico-chemical oscillations*, Discussion Meeting, Deutsche Bunsen Gesellschaft für Physikalische Chemie, Aachen, vol. 1, p. 83
- Orbon M, Körös E and Noyes R M 1979 *J. Phys. Chem.* **83** 3056
- Ramaswamy R and Lalitha P V 1990 *Bull. Electrochem.* **6** 339
- Rastogi R P and Srivastava P K 1987 *J. Non-Equil. Thermodyn.* **12** 123
- Sandell E B and Onishi H 1978 *Potentiometric determination of trace metals: General aspects* (New York: John Wiley) pp. 662–63
- Srivastava P K, Mori Y and Hanzaki I 1991 *Chem. Phys. Lett.* **177** 213
- Tockstein A and Handlirova M 1979 *Kinetics of physico-chemical oscillations*, Discussion Meeting, Deutsche Bunsen Gesellschaft für Physikalische Chemie, Aachen, vol. 1, p. 142