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A Study of Self Oscillatory Chemical Reaction of Gallic Acid and Potassium Bromate System

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Synopsis. The oscillatory phenomenon during oxidation of gallic acid with potassium bromate, catalyzed by cerium ion in acid medium with stirring was investigated. The cross section of a three dimensional graph for the regions where the oscillatory behavior can be observed is given. Effect of Ag^+ and Br^- on the oscillatory behavior was studied.

Oscillation in the concentrations of Br^- and Ce^{4+}/Ce^{3+} during the oxidation of malonic acid by bromate ion with cerium ion as a catalyst was studied by different workers.[1-7] Similar oscillatory phenomenon was observed in gallic acid-bromate system catalyzed by cerium ions.

Experimental

A freshly recrystallized gallic acid (GA)(Riedel), 1,10-phenanthroline ferrous sulphate complex (ferroin) solution (0.025 M)(BDH) and other BDH AR grade chemicals were used. A requisite quantity of gallic acid was dissolved in distilled water, to which a ceric solution with sulphuric acid was added. The reaction was studied at constant temperature and with constant moderate stirring on addition of a requisite volume of bromate solution and a drop of ferroin indicator, the total volume being kept 10 ml. The color change from red to green, *i.e.*, Ce(III) to Ce(IV), takes place abruptly. The oscillations visually observed are reporducible within the limits of experimental error.

Results and Discussion

Important parameters for the occurrence of oscillations in the system are bromate, gallic acid and cerium ion concentrations. A minimum concentration of acid which depends upon the concentration of other reactants, is required to start the reaction. When the reactant concentrations are kept constant, the frequency of oscillations (n) increases, and the total time of oscillation (T) decreases with increasing acid concentration. A large number of oscillations were observed at an acid concentration of 2.57 N.

Effect of Individual Reactant. (Other Variables Being Kept Constant).

(a) Gallic Acid Variation.

($[BrO_3^-]=0.1$ M, $[Ce(IV)]=0.003$ M, $[acid]=2.57$ N). The total number of oscillations (N) is high at concentration of 0.03 M, and decreases when the concentration becomes greater or smaller than this value. The value of n decreases and T increases with a decrease in gallic acid concentration.

(b) Bromate Variation.

($[GA]=0.04$ M, $[Ce(IV)]=0.001$ M, $[acid]=2.57$ N). The value of N is maximum for $[BrO_3^-]=0.1$ M. Values of n and I (induction period) decrease while T increases when $[BrO_3^-]$ increases.

(c) Cerium Ion Variation.

($[GA]=0.04$ M, $[BrO_3^-]=0.1$ M, $[acid]=2.57$ N). In the concentration range $3.0\times10^{-4}-1.0\times10^{-4}$ M, a great number of oscillations were observed and outside the range the value of N decreased. With increase and decrease in concentrations of total cerium ion beyond the mentioned range, the n value increased and decreased respectively. The system showed 80 oscillations in 150 min before the oscillation ceased, when $[GA]=0.045$ M, $[BrO_3^-]=0.1$ M, $[Ce(IV)]=3.0\times10^{-4}$ M and $[acid]=2.57$ N.

The oscillatory cycle can be divided into two processes, the former is a trigger process and the latter is a recovery.

$$Ce^{3+} \xrightarrow[H^+]{BrO_3^-} Ce^{4+} \qquad (1)$$

$$Ce^{4+} \xrightarrow{GA} Ce^{3+} \qquad (2)$$

The products of bromate reduction in the trigger process (1) may brominate gallic acid. Bromide ion is formed as a result of decomposition of gallic acid-bromine derivatives induced by ceric ion oxidation (2). It was verified experimentally that bromide ion is a strong inhibitor of trigger process. Addition of Br^- inhibits the trigger process, resulting in the dampening of oscillation. At 0.005 M of $[Br^-]$, inhibition of oscillatory behavior was observed. Addition of Ag^+ which removes Br^- also dampens down and at 0.1M concentration inhibits the oscillation. This indicates that $[Br^-]$ plays an important role in the oscillatory behavior[7] (Fig. 1).

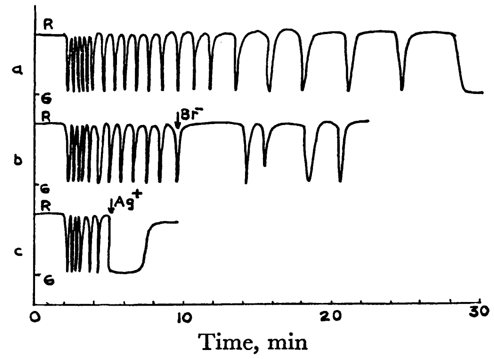

Fig. 1. Oscillatory curve with respect to time. (As indicated by ferroin.) R- Red and G- Green representing Ce(III) and Ce(IV) respectively.
(a) $[GA]=0.0425$ M, $[BrO_3^-]=0.1$ M, $[Ce(IV)]=0.0005$ M and $[acid]=2.57$ N.
(b) Effect of bromide ion. Concentrations similar as in (a) and $[KBr]=0.05$ M.
(c) Effect of silver ion. Concentrations similar as in (a) and $[AgNO_3]=0.05$ M.
Arrow indicates the point of addtion.

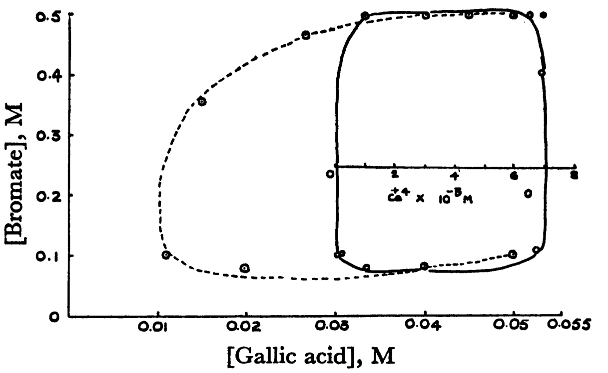

Fig. 2. Cross sections of three dimensional plot for the boundary region where oscillations are observed. Temperature 35 °C. [Sulfuric acid] 2.57 N. [GA]—X axis, [BrO_3^-]—Y axis and [Ce(IV)]—Z axis.
------ represents the curve of [GA] *vs.* [BrO_3^-].
—— represents the curve of [Ce(IV)] *vs.* [BrO_3^-] when [GA]=0.04 M.

Oscillations could be observed in the concentration range of reactants studied (Fig. 2). The boundary conditions of gallic acid, bromate and cerium ion concentrations were determined keeping temperature, acidity and stirring constant. The upper limit of [GA] could not be fixed due to its solubility limitation. As the concentrations of reactants approach the boundary conditions, the oscillations tend to cease and beyond it, they are not significant.

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