COBALT ION CATALYSED SELF OSCILLATORY REACTION IN CLOSED SYSTEM OF POTASSIUM BROMATE AND GALLIC ACID

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(*Received 10 December 1975*)

An oscillatory behaviour in the concentration of Co(II)-Co(III) was observed in gallic acid-potassium bromate system in sulphuric acid medium. Effect of variation of concentration of reactants and acid including the role of Br^- in the system was studied.

INTRODUCTION

Oscillatory behaviour in the coupled reactions of '*Beloussov Reaction*' type (in the concentrations of bromide and ceric ion) during the oxidation of malonic acid by bromate, catalysed by cerium ion in acid medium was studied intensively. Similar phenomenon can be observed by substituting malonic acid with any carboxylic acid of configuration R-CO-CH_2-COOH, and Ce(III)-Ce(IV) couple by Fe(II)-Fe(III) or Mn(II)-Mn(III) couples (Chance *et al.* 1971). Similar behaviour was also reported by employing, 2,4-pentone dione (Koros *et al.* 1973) and gallic acid (Sreekantha Babu *et al.* 1976) instead of malonic acid in the above system.

The periodic variation in concentration of Co(II)-Co(III) during the oxidation of gallic acid by bromate in presence of cobalt ion has been investigated potentiometrically at 35°C and presented in this communication.

MATERIALS AND METHODS

Systronics Type 322-1 pH meter for potentiometric studies with Pt-Pt electrodes was used to follow the reaction.

A freshly recrystallised gallic acid (Reidel) was used and all other reagents are of B.D.H. AR grade chemicals.

The oscillatory behaviour depends upon the concentrations of bromate, gallic acid, cobalt ion and also on acid concentration primarily, although stirring and temperature influence it to some extent.

Taking weighed amount of gallic acid in known volume of water, cobalt nitrate solution was added to it followed by sulphuric acid. The reaction was started by the addition of bromate solution maintaining total volume of solution to 20 ml with moderate constant stirring and potential variations were noted from the time of addition of bromate ion to the system.

RESULTS AND DISCUSSION

Due to complexity of the reaction, the influence of each reactant was studied by keeping the molar concentrations of the remaining reactants unaltered in the solution.

Keeping initial concentrations of gallic acid = 0.041M; potassium bromate = 0.1M and sulphuric acid = 2.8 N, the effect of variation in cobalt ion concentration from 0.0025M to 0.02M was studied with 0.01M $Co(NO_3)_2$. The system gave a high number of steady state oscillations with other concentrations, the number of oscillations being less or reaction being rather fast.

When initial concentration of bromate = 0.1M; $Co(N_3O_3)_2$ = 0.01M and acid= 2.8 N were maintained the decrease in gallic acid concentration from 0.041M to 0.0053M reduced the total number of oscillations and total time (for oscillations could be observed). Higher concentration limit could not be studied due to its solubility limitations to give a homogeneous solution.

Maintaining the initial concentrations of gallic acid=0.041M; $Co(NO_3)_2$=0.01M and acid = 2.8N, the increase in bromate concentration from 0.1M to 0.2M increased the frequency of oscillations decreasing the total time for oscillation to occur. With the decrease in concentration of bromate to 0.06 M only one oscillation was observed after four minutes. Similar observations were noticed with gallic acid of 0.03M and other reactant concentrations as above.

When two sets of reaction mixtures with two initial concentrations of gallic acid = 0.03M and 0.041M; bromate = 0.1M and $Co(NO_3)_2$ = 0.01M were taken, steady oscillations were observed in the range of 2.14N to 3.22N sulphuric acid concentration. Below this range the frequency of oscillations is low while at high acidities frequency is high and for both the cases total time during which oscillations occur is less.

The oscillatory cycle can widely be divided into two reactions, i.e., trigger and recovery reactions. In the former one, Co(II) is oxidised to Co(III) by bromate forming Br^- also:

$$Co^{2+} \xrightarrow[H^+]{BrO_3^-} Co^{3+} \; ; \qquad \ldots \; (1)$$

and in the later reaction Co(III) is reduced to Co(II) by gallic acid

$$Co^{3+} \xrightarrow{GA} Co^{2+} \qquad \ldots \; (2)$$

It appears that Br^- plays a role in the oscillatory behaviour of this system. The role of Br^- was studied by increasing its concentration. High concentration of Br^- dampens the reaction probably due to the dampening of the trigger reaction. This is further confirmed by addition at Ag^+ to remove the Br^-. Addition of Ag^+ to remove Br^- also inhibits the reaction if its concentration is high and dampens down the oscillation if it is low.

ACKNOWLEDGEMENTS

The authors are thankful to Council of Scientific and Industrial Research, India for providing Post-doctoral fellowship to one of them (J.S.) and to Prof. M.M. Bokadia, Head, School of Studies in Chemistry for his keen interest in the progress of work and providing the laboratory facilities.

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