Uncatalyzed Chemical Oscillatory Behavior in the Oxidation of Catechol with Acidic Bromate Solution

Punnappillil K. R. Nair,* Archana Mittal, and Kotra Srinivasulu

School of Studies in Chemistry, Vikram University, Ujjain, 456-010, India

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Synopsis. A temporal oscillatory behavior of the redox potential in the oxidation of catechol with potassium bromate in sulfuric acid medium is reported.

Uncatalyzed temporal oscillations in bromide ion concentration and redox potential in the oxidation of phenols and anilines with acidic bromate solution have recently been reported by M. Orban and E. Koros, who claim that chemical oscillations do not take place in the oxidation of catechol.[1–3] Our observation shows that catechol is a better substrate to exhibit oscillations in their oxidation with acidic bromate at appropriate concentrations of the reactants. The effect of different catalysts on the system was also observed.

Experimental

Catechol (BDH) was purified by sublimation, $KBrO_3$ (Reidel), H_2SO_4 (BDH) and 1,10-phenanthroline iron(II) sulfate complex (ferroin, BDH) were used. All the solutions were prepared in conductivity water.

Freshly prepared catechol solution (0.25 M†) and H_2SO_4 (18 M) were mixed in a reaction cell thermostated at room temperature (30±0.5 °C) and the reaction was initiated by addition of the required amount of potassium bromate solution (0.4 M). Total volume was kept 25 ml in all cases by addition of the required amount of conductivity water. The reaction was monitored by noting the potential changes from a Systronics (India) pH meter, type 322-1 using Pt–Pt electrodes.[4] In the case of catalysed systems the catalysts were added just before the addition of bromate. Observation was made without stirring, since stirring was found to interfere with the reaction. The boundary concentrations for each reactant to exhibit oscillations were determined by altering the concentration of one of the reactants and keeping that of the rest unaltered. The results are reproducible within the limits of experimental error.

Results and Discussion

Chemical oscillation takes place over narrow ranges of concentration of the reactants, *i.e.* catechol (0.015—0.080 M), bromate (0.048—0.128 M), and acid (0.36—2.88 M). The optimum concentrations for maximum number of oscillations: catechol (0.05 M), bromate (0.096 M), and acid (1.8 M). The oscillations were observed for more than 4 h with decreasing amplitudes as the reaction proceeds (Fig. 1A). Increase in concentration of catechol, bromate or acid, within the boundary conditions, diminished the induction period. Though the reaction starts after the addition of bromate, the oscillatory behavior starts only after an induction (preoscillatory) period of *ca.* 70 min. However, a dark colored species appearing in the system after the addition of bromate vanishes quickly, with a definite potential change.

According to Orban and Koros[2,3] oxidation of catechol with acidic bromate results in the formation of a stable quinone and bromine and thus oscillations do not take place. Though a dark colored species, probably quinone, is formed in the system after bromate addition, it disappears quickly, indicated by the sudden disappearance of the dark color with simultaneous potential change, in the concentration ranges in which reactants exhibit oscillatory behavior. However, the quinone turns into a black or brown precipitate on either side of the boundary conditions of the reactants showing oscillatory behavior. Though bromine is produced in the system, it is consumed probably by brominating the substrate, as evidenced by the gradual disappearance of the brown color from the system before oscillatory behavior appears.

The oscillatory behavior is strongly inhibited by stirring of the reaction mixture; an insignificant number of oscillations could be observed even with slower stirring rate. Inhibitory role of stirring on oscillatory behavior in $BrCH(COOH)_2/BrO_3^-/H_2SO_4/Ce$ system was also reported by Sorensen.[5]

Effect of Catalysts. Belousov-Zhabotiniskii (BZ) catalysts, (Ce(IV), Mn(II), and ferroin) can catalyse the system, ferroin being found to be the most effective one. Introduction of a catalyst decreases the preoscillatory period, while the frequency, number of oscillations and total time for exhibiting oscillations (life time) increase with a slight increase in the amplitude of oscillations (Fig. 1B). Revival of oscillations take place by the introduction of catalyst (2×10^{-4} M ferroin) when the oscillations become insignificant in both uncatalyzed and catalyzed systems. However, no regeneration of oscillations of this type was observed when the catalyst was added at a later stage.

Effect of Halide Ions: Addition of Cl^-, Br^-, or I^- inhibits the reaction. Above 10^{-4} M all the ions inhibit the number and shape of the oscillatory cycles. The inhibitory effect of Cl^- is most prominent.

Effect of Silver Ion: Removal of bromide ions from the system by precipitation of AgBr with Ag^+ ($AgNO_3$) has a pronounced effect on the reaction. By partial removal of bromide ions the oscillations continue, while complete removal inhibits the reaction strongly.

Effect of Radical Scavenger: Addition of acrylonitrile after addition of bromate or in between oscillations suppresses the behavior.

Similar to BZ reaction the uncatalysed bromate oxidation of catechol is controlled by bromide ion and inhibited by chloride ion. The reaction can be explained by means of the Field, Koros and Noyes mechanism,[6] by considering the fact that catechol plays the role of substrate as well as catalyst. The reaction might consist

† 1 M=1 mol dm^{-3}.

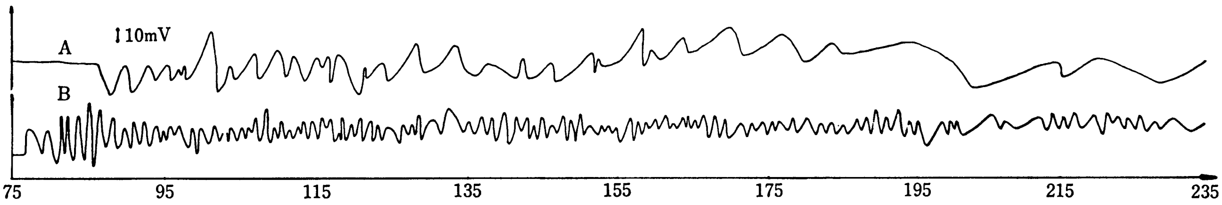

Fig. 1. Oscillatory behavior of the redox potential in the oxidation of catechol with acidic bromate solution.
A. Uncatalyzed system: catechol (0.05 M), bromate (0.096 M), and acid (1.8 M).
B. Catalyzed system: catechol (0.05 M), bromate (0.096 M), acid (1.8 M), and ferroin (2×10^{-4} M).

of two steps of kinetics, the oxidation of catechol by bromate with the subsequent reduction of the latter to bromide ions and bromination of the aromatics. The source of bromide ions for the continuance of the reaction is the brominated products of the aromatics. Brominated products of catechol, *o*-benzoquinone, and 3-bromo-*o*-benzoquinone have been separated from the butanol extract of the reaction mixture by chromatography. So far no bromine has been observed in the BZ reaction.[7,8] However, bromine has been observed in the oscillatory oxidation of catechol.

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