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Insights into Chemical Oscillatory Reactions through an Illustrious Case Study of p-Sulphonic Phenol: Sulphuric Acid: Bromate System

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ABSTRACT

The present paper describes the optimum and boundary conditions for uncatalyzed temporal oscillations in the redox potential in the oxidation of p-sulphonic phenol in acidic bromate (H_2SO_4). The presence of sulphonic acid group in the aromatic ring is found to have a significant influence on the oscillatory behavior of phenol. Moreover, it was also interesting to note that the catalyst Ferrioin has been found to enhance the oscillatory behavior.

Keywords: complex reactions, UBO, p-sulphonic phenol, uncatalysed system, effect of ferrioin

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INTRODUCTION

After doing work on chemical oscillatory reactions everybody always becomes interested in applying insights and techniques from his studies of various systems, to systems of significance in other areas, particularly biology. Part of the interest in chemical oscillating reactions grew from the study of non-linear dynamics applied to physics and biology, even meteorology and economics. The connection between the life process that exhibits oscillating behavior and chemical oscillating system is also one of the most interesting study subjects. An important, unifying discovery is that many complex natural phenomena are governed by simple dynamic laws. Chemical oscillating reactions are no exception, because they exhibit complex behavior often based on relatively simple dynamic rules. Among existing chemical oscillators, the vast majority relies on a few elements that possess multiple oxidation states, such as halogens, sulfur and some transition metals. The first report of Bromine giving multiple oxidation states was done by B. P. Belousov [1] and A. M. Zhabotinsky [2] using malonic acid/ H_2SO_4 /Cerium/ BrO_3^- . In 1978, Orban and Koros [3] carried out an extensive search to explore chemical oscillations in the oxidations of aromatic compounds having hydroxyl or amine group by acidic bromate. Because of the absence of metal catalysts, systems are referred to as Uncatalysed Bromate Oscillators (UBOs) in which the parallel reaction of oxidation and bromination of the organic substrate takes place.

To explain the mechanism of UBOs [4] it was assumed that substrate should be a hydroxy benzene in which ortho and/or para positions should be free. For this reason it was assumed that hydroxy aromatics having ortho or para position unoccupied show oscillatory behaviour and even the preoccupation at these positions by another hydroxyl group was also considered not to show the behaviour. However, later we could find [5-11] that ortho or para di hydroxy benzenes showed the oscillatory behaviour during their acidic bromate oxidation. All these observations led us to conceive the idea that the hydroxy aromatics show oscillatory behaviour which have atleast one ortho or para position is unoccupied or these positions are preoccupied by hydroxy group during their acidic bromate oxidation.

In the present paper p-sulphonic phenol is a reducing agent popularly known as substrate, in which only one $-\text{OH}$ group is present and para position occupied by $-\text{SO}_3\text{H}$ group. So the possibility of forming p-quinone is not there. However there is every possibility of forming o-quinone, as both the ortho positions are free.

The use of sulphonic acid and its salts to improve the washfastness of dyes due to their capability of binding more tightly to the fabric and their vast use in detergent industry makes p-sulphonic phenol an important compound to be studied.

EXPERIMENTAL

All the chemicals used were of high purity. The reaction was monitored on a PM 2522 Philips VA Ω multimeter using bright Pt-Pt electrodes [1, 2]. The reaction was found to be sensitive to stirring hence the solution was stirred at 50 rpm. While preparing the reaction mixture H_2SO_4 was added after the addition of water. Total volume was kept 25 ml in each case. All the experiments are carried out at $30^\circ \pm 0.05\text{C}$.

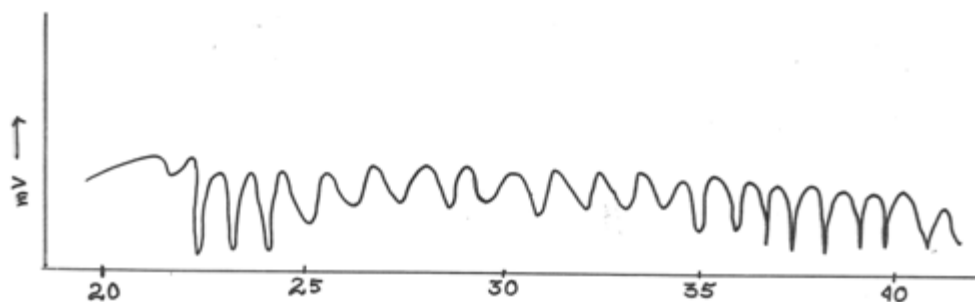
RESULTS AND DISCUSSION

In this system no dark colour is produced after the addition of bromate solution. However the intensity of orange colour of the reaction mixture increased during the induction period. The studies were carried out under slow stirring conditions since fast stirring inhibited the reaction while in unstirred system few chaotic oscillations appeared.

Similar to other bromate driven oscillators the oscillatory behaviour is specific to the initial concentration of the reactants. The oscillations could be observed if $0.008 \text{ M} \leq [\text{p-sulphonic phenol}] \leq 0.028 \text{ M}$ when $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$ and $[\text{BrO}_3^-] = 0.032 \text{ M}$. With the increase in the concentration of p-sulphonic phenol induction period increased but at $[\text{p-sulphonic phenol}] > 0.02 \text{ M}$ no change in the induction period was observed. Beyond this concentration the number of oscillations decreased. Oscillations were observed only if $0.54 \text{ M} \leq [\text{H}_2\text{SO}_4] \leq 1.98 \text{ M}$ when $[\text{p-sulphonic phenol}] = 0.02 \text{ M}$ and $[\text{BrO}_3^-] = 0.032 \text{ M}$. The increase in the concentration of H_2SO_4 brought a gradual decrease in induction period and an increase in frequency of oscillations. At greater acidities the amplitude was decreased. When $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$ maximum 22 oscillations were observed. In the similar way oscillations were only observed if $0.024 \text{ M} \leq [\text{BrO}_3^-] \leq 0.040 \text{ M}$ at $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$ and $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$. The optimum concentration of bromate was found to be 0.032 M . The induction period decreases with the increase in the concentration of bromate. (Fig. 1)

Figure 1:

p-sulphonic phenol/ H_2SO_4 / BrO_3^- system (slow stirred)
 $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$, $[\text{BrO}_3^-] = 0.032 \text{ M}$



At this optimum concentration of p-sulphonic phenol/sulphuric acid/bromate system if p-sulphonic phenol is replaced by Phenol no oscillations were observed and precipitate appeared. This shows a pronounced effect of the presence of sulphonic acid group at para position in Phenol.

Effect of stirring

The effect of rate of stirring is much pronounced on the system. When the reaction was carried out at a speed 50 rpm at $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44$ and $[\text{BrO}_3^-] = 0.040 \text{ M}$, 22 oscillations were observed after an induction period of 1275 secs with a frequency of $1.09 \text{ oscillations min}^{-1}$. Under the same concentration conditions, if the

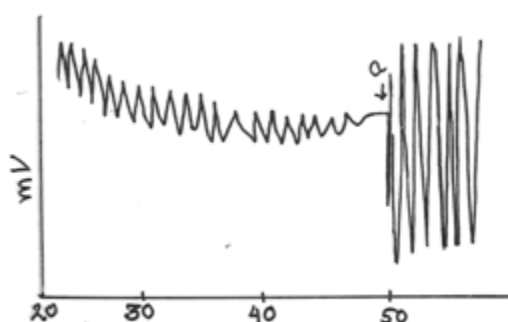
reaction mixture is stirred only initially to make the reaction mixture homogenous, only 11 oscillations appear with a reduction of a frequency to 0.6 oscillations min^{-1} , while the induction period increases to 1680 secs. If the rate of stirring is increased to 150 rpm under the same concentration conditions, oscillations didn't appear at all.

Effect of Ferroin

When $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$ and $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$ and $[\text{BrO}_3^-] = 0.040 \text{ M}$, Ferroin was found to inhibit the oscillatory behaviour. However if the concentration of all the reactants was halved i.e. $[\text{p-sulphonic phenol}] = 0.010 \text{ M}$ and $[\text{H}_2\text{SO}_4] = 0.72 \text{ M}$ and $[\text{BrO}_3^-] = 0.020 \text{ M}$, addition of $[\text{Ferroin}] = 1 \times 10^{-4} \text{ M}$ brought 23 oscillations after 480 secs with an increase in frequency to 3.2 oscillations min^{-1} , the stirring rate was 50 rpm. The Ferroin catalyzed system in also inhibited by fast rate of stirring and only a few oscillations with low amplitude are observed. (Fig. 2)

Figure 2:

p-sulphonic phenol/ H_2SO_4 / BrO_3^- system (slow stirred) (revival of oscillations)
 $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$, $[\text{BrO}_3^-] = 0.032 \text{ M}$
 At point 'a' $[\text{ferroin}] = 1 \times 10^{-4} \text{ M}$ added



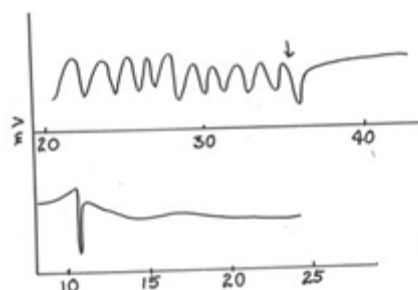
Our experiments with N_2 gas bubbling gave the same results i.e. few oscillations of low amplitude, which may be attributed to slower/ faster rate of Bromine expulsion than is required.

Effect of Bromine and radical scavenger

In the reaction system containing $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$ and $[\text{BrO}_3^-] = 0.040 \text{ M}$, 0.75 ml of Allyl alcohol, a Br_2 scavenger, completely inhibited the oscillations, which explains the role of Br_2 in the reaction [12]. In the same way 0.25 ml of Acrylo-nitrile completely inhibited the oscillations, which explains the free radical mechanism suggested by Field, Koros and Noyes. (Fig. 3)

Figure 3

p-sulphonic phenol/ H_2SO_4 / BrO_3^- system (slow stirred)(Effect of Allyl alcohol)
 $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$, $[\text{BrO}_3^-] = 0.032 \text{ M}$
 At point 'a' 0.75 ml of 1% allyl alcohol added
 At point 'b' 0.75 ml of 1% allyl alcohol added
 (Note: same trend with Acrylo nitrile)

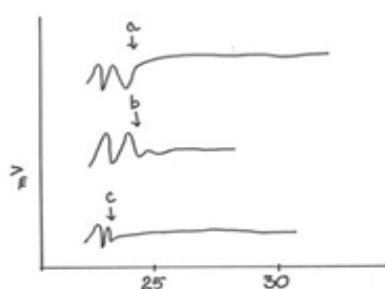


Effect of inhibitors

In the reaction mixture containing $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$ and $[\text{BrO}_3^-] = 0.040 \text{ M}$, $[\text{Cl}^-] = 4 \times 10^{-4} \text{ M}$, $[\text{Br}^-] = 4 \times 10^{-4} \text{ M}$ and $[\text{Ag}^+] = 4 \times 10^{-4} \text{ M}$ inhibited the oscillatory behaviour completely [12]. (Fig. 4)

Figure 4:

p-sulphonic phenol/ H_2SO_4 / BrO_3^- system (slow stirred) (effect of inhibitors)
 $[\text{p-sulphonic phenol}] = 0.020 \text{ M}$, $[\text{H}_2\text{SO}_4] = 1.44 \text{ M}$, $[\text{BrO}_3^-] = 0.032 \text{ M}$
 At point 'a' $[\text{AgNO}_3] = 4 \times 10^{-4} \text{ M}$ added
 At point 'b' $[\text{KBr}] = 4 \times 10^{-4} \text{ M}$ added
 At point 'c' $[\text{KCl}] = 4 \times 10^{-4} \text{ M}$ added



All these experimental results could be explained on the basis of OKN [4] mechanism. In which the presence of $-\text{SO}_3\text{H}$ group, which is an electron withdrawing group, enhances the scillatory behaviour of hydroxy benzene. Similar result was observed with Catechol [7] and Tiron [6] systems. Tiron gave a large number of oscillations as compared to Catechol. Which can be attributed to the presence of two $-\text{SO}_3\text{H}$ groups in tiron.



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