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A SIGNIFICANT CASE STUDY OF UNCATALYSED BROMATE OSCILLATOR THROUGH THE TEMPERATURE EFFECT DURING ACIDIC BROMATE OXIDATION OF CATECHOL

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Abstract: Catechol-Sulphuric acid-Bromate system is a well known uncatalysed bromate Oscillator (UBO). The system is highly sensitive towards an increase in temperature above 303 K. The parameters during the present study *viz.* induction period and period of oscillations decreased as temperature was increased. Further, as evident during the estimation of apparent energy of activation the graph between log 1/t vs 1/T has shown prominent effect and preview of such responses.
Keywords: Uncatalysed bromate Oscillator (UBO), catechol, temperature effect, apparent energy of activation.

Introduction

The dimensions of non-equilibrium chemistry, especially the study of systems far from equilibrium, are growing continuously on account of interests in real systems such as living systems. The Bromate driven chemical oscillators are among one of the most complicated chemical systems which are far from equilibrium. Belousov-Zhabotinskii reaction, catalysed and uncatalysed, is most studied one which involves bromine chemistry [1-3]. The uncatalysed bromate oscillators do not involve any metal ion catalyst and the organic substrate, usually a phenol or an aniline derivative, plays the role of catalyst as well [4-6]. The mechanism of these bromate oscillators can be explained by modified FKN mechanism known as OKN mechanism [7]. A number of studies have been carried out on the effect of temperature on BZ reaction [8-19]. If the system under examination can be in various oscillatory dynamic states, the apparent activation energies corresponding to different pathways may be of crucial importance for this purpose. In that case the activation energies can be determined by means of the main characteristics of the oscillatory process such as pre-oscillatory period, total duration of the oscillatory period, the period from the commencement of oscillations to a certain number of oscillations, total number of oscillations and others.

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In the present paper an attempt has been made to determine the apparent energy of activation of the overall process at the optimum concentration conditions of the Catechol-H_2SO_4-BrO_3^- system [20] in the absence of catalyst i.e. UBO. Studies have been carried out over a temperature range of 303 K to 323 K with respect to its effect on different oscillatory parameters like induction period and time period for fixed number ososcillations.

Experimental

All the chemical used were of high purity. The reaction was monitored on a PM 2522 Philips VA Ω multimeter using bright Pt-Pt electrodes. The reaction was found to be sensitive to stirring hence the solution was stirred only for 5 seconds after the addition of bromate solution. The total volume was kept 25 ml in each case. Studies are carried out at [Catechol] = 0.05 M, [H_2SO_4] = 0.80 M and [BrO_3^-] = 0.096 M [20], which is optimum concentration condition for this system to get maximum number of oscillations.

Result and Discussion

The Catechol-H_2SO_4-BrO_3^- system is found to be sensitive to increase of temperature similar to other bromate oscillators. The effect of increase of temperature on various parameters is summarized in Table 1.

Table 1: Effect of increase of temperature

Temperature (K)	1/T x 10^{-4}	Induction Period (seconds)	't' Time taken for first 10 oscillations (seconds)	log 1/t sec^{-1}
303	33.01	5090	2695	-2.432
313	31.96	2230	1265	-2.102
323	30.96	780	650	-1.812

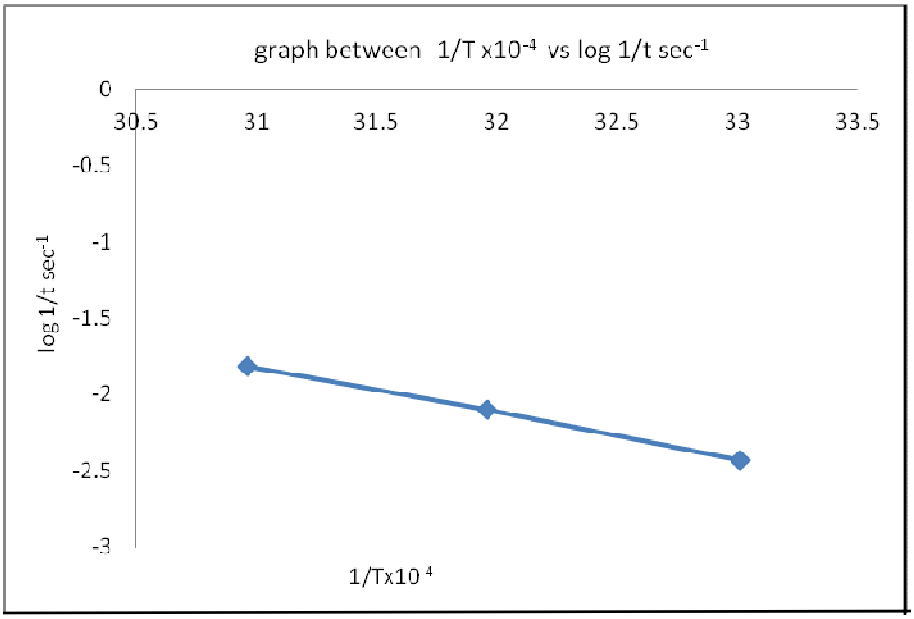
It is observed that induction period and time period of first 10 oscillations decrease with increase in temperature.

The decrease in induction period with the increase in temperature can be attributed to the increase in the rate of formation of a critical amount of bromo derivative of substrate. The decrease in induction time shows a linear relationship with temperature.

The decrease in the time period for first 10 oscillations may be explained as the rate of reaction increases with the increase in temperature, so the oscillations take lesser time to occur.

At 303 K no turbidity appears during the oscillatory phase of reaction. However at temperature 313 K a turbidity appears after about 20 oscillations. While at 323 K turbidity appeared after about 15 oscillations. At temperatures > 323 K turbidity appears at an early stage of the reaction hence experiments were not be carried out above this temperature.

The apparent energy of activation was found to be 13.78 K Cal mol^{-1} which is less than the apparent energy of activation for Phenol system [21]. This decrease in apparent energy of activation can be attributed to extra steps to be carries out in phenol system to introduce second hydroxy group in the benzene ring.



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