Uncatalysed oscillations in the bromate – pyrogallol system

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Abstract. Studies on the bromate-pyrogallol system with sulphuric and perchloric acids are presented. The addition of acrylamide and acrylonitrile to the oscillatory system indicates the presence of free radicals. The apparent energy of activation for the overall process is 10.1 ± 1 and 20 ± 0.5 kcal mol^{-1} respectively for sulphuric and perchloric acids. The static potential measurements with different constituents together with double recording of oscillations with a platinum and Ag/AgBr indicator electrode establish that oscillations are caused by continuous change in the concentration of bromine and bromide ions.

Keywords. Oscillatory reaction; periodic reaction; uncatalysed oscillations; bromate-sulphuric acid/perchloric acid-pyrogallol system; effect of monomer; activation energy.

1. Introduction

Oscillatory reaction in the bromate system with Mn^{2+}/Ce^{3+} has been extensively studied (Noyes and Field 1977; Ganapathisubramanian *et al* 1980). Pyrogallol gives oscillations in the bromate system without the presence of metal ion (Orban and Koros 1978). The addition of [iron (1, 10 phenanthroline)$_3$]$^{2+}$ or [Ru ($\alpha\alpha'$ dipyridyl)$_3$]$^{2+}$ has been reported to inhibit the oscillations (Orban and Koros 1979).

2. Experimental

Sulphuric acid and pyrogallol were taken in a polythene beaker and thermostated. Thermostated potassium bromate was added to trigger off the oscillations. The oscillations were followed by continuous recording of the potential between a platinum indicator electrode and a saturated calomel electrode connected through a potassium nitrate bridge. The solution was well-stirred for homogeneity with a magnetic stirrer. The difficulty in obtaining reproducible results in the iodate and bromate systems had been overcome by the choice of the reaction vessel and the pretreatment of the electrode (Ramaswamy *et al* 1978, 1980).

3. Results and discussion

The concentration of the constituents have a profound influence on the oscil-

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latory behaviour of the system and help in identifying the species causing the oscillations. The addition of acrylonitrile or acrylamide affects the oscillatory pattern of the systems differently.

The apparent energy of activation for the overall process has been evaluated. The double recordings obtained with platinum and Ag/AgBr indicator electrodes and the static potential measurements with different compositions of the constituents enable identification of the species causing the oscillations.

Simulation of oscillatory pattern by the periodic addition of a constituent provides visual and direct evidence of the conclusions drawn in identifying the species causing oscillations.

3.1 Effect of concentration

3.1.a Pyrogallol concentration : The concentration of pyrogallol was varied in the range 0.03 to 0.08 M with constant concentrations of potassium bromate (0.1 M) and sulphuric acid (2 M) at 30°C. Eleven oscillations were recorded in 2 min at 0.03 M with an induction time of 0.33 min. The number of oscillations decreased to 4 in 6.5 min at 0.07 M. The system did not oscillate at 0.08 M pyrogallol. The range of concentration of pyrogallol in which the system gives oscillations with perchloric acid (3.22 M) and potassium bromate (0.1 M) at 30°C is 0.3 to 0.06 M. Standard conditions produced ten oscillations in 6.5 min with an induction time of 1.2 min (figure 1). The optimum con-
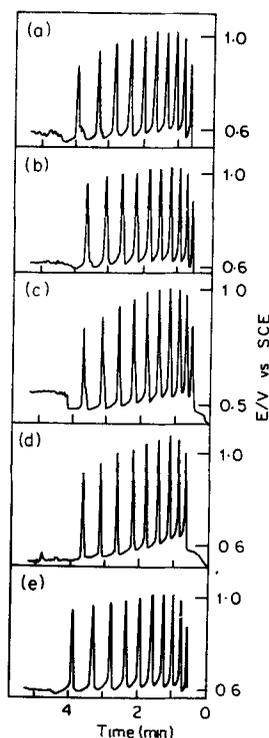

Figure 1. Reproducibility of oscillations of the pyrogallol-sulphuric acid-bromate system. Bromate = 0.1 M; pyrogallol = 0.05 M; Sulphuric acid = 2 M; temperature 30°C.

centrations of pyrogallol employed in subsequent studies were 0.05 M and 0.06 M in sulphuric acid and perchloric acid systems respectively.

3.1.b Bromate concentration : The concentration of potassium bromate was varied in the range 0.06 to 0.16 M. The optimum concentration of potassium bromate employed subsequently for both the systems was 0.1 M.

3.1.c Acid concentration : Sulphuric acid concentration was varied in the range 1 to 3 M, while that of perchloric acid from 3 to 3.7 M. There was a decrease in the amplitude and increase in the frequency of oscillations at higher concentrations of the acids. The concentration of sulphuric and perchloric acids employed for detailed study were 2 M and 3.6 M respectively. Ten oscillations in 4 min and 23 oscillations in 2.7 min were observed under these conditions respectively with the two systems.

3.2 *Effect of temperature*

The reaction was studied in the temperature range 5 to 60°C for both systems. Increase in temperature resulted in an increase in frequency of oscillations and the amplitude. The amplitude increased from 200 mV at 5°C to 430 mV at 48°C in the sulphuric acid system. The apparent energy of activation for the overall process has been evaluated (Ganapathisubramanian *et al* 1978) from the linear plot of log $1/t$ *vs* $1/T$ on the basis that the rate constant is inversely proportional to time (t). For this purpose, the total duration, oscillating time and the time for a definite number of oscillations were considered. The apparent energy of activation for the overall process respectively for sulphuric acid and perchloric acid systems are 10.1 ± 1 and 20 ± 0.5 kcal mol^{-1}.

3.3 *Effect of monomers*

The addition of arcylonitrile to the pyrogallol-bromate-sulphuric acid system reduced the amplitude to a considerable extent. After the termination of the oscillations the reaction mixture yielded, on standing, a solid non-polymeric precipitate. The IR spectrum of the compound indicated the presence of a cyano group.

3.3a *Addition of acrylamide :* The addition of acrylamide to the system brought about a considerable change in the oscillatory behaviour. Acrylamide (1 ml of 5% solution) added before the start of the oscillations increased the duration of oscillation from 4 to 7 min. However the duration decreased to 1.2 min for an addition of 2 ml acrylamide. The same trend was maintained when the addition of acrylamide was made 1 min after the start of the reaction. The response of the oscillatory system to the addition of different amounts of acrylamide after the first oscillation is presented in figure 2. The pattern is characterised by double peaks in the presence of acrylamide and the peak shoulder position shifts with the addition of different amounts of acrylamide.
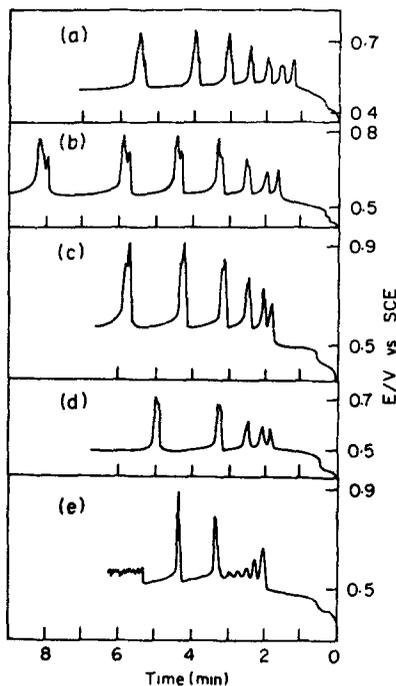
Figure 2. Effect of addition of acrylamide on bromate pyrogallol-perchloric acid system after the first oscillation.

Bromate = 0.1 M; Pyrogallol = 0.06 M; Perchloric acid = 3.22 M; Temperature 30°C. Acrylamide (5% solution) added (ml) a. 2.5, b. 1.0, c. 0.5, d. 0.3, e. nil.

3.4 Species causing oscillations

The oscillations recorded with Ag/AgBr indicator electrode establish that the concentrations of bromide are 10^{-6} and 10^{-5} M at the peak and base regions respectively. Static potential values of the platinum electrode measured with different constituents present show that in the binary system with a constant bromide concentration of 10^{-3}M, the potential was 0.14 V (vs SCE) with 10^{-5} M bromine and 0.8 V (vs SCE) with 10^{-4} M bromine. The potential of the platinum electrode with the oxidised product of pyrogallol is 0.25 V (vs SCE).

The addition of ferroin (0.002 M) or iron $\alpha\alpha'$ dipyridyl (0.002 M) to the uncatalysed bromate system leads to a switch over of the oscillations to a new oscillatory phase with an amplitude of about 100 mV in the range of 0.95 to 1.05 V (vs SCE). The exchange current density for Pt/Br$_2$/Br$^-$ is about 10^{-5}

amp/cm^2 and for Pt/Fe^{3+}/Fe^{2+} is nearly 10^{-3}amp/cm^2. The oscillatory behaviour of the system is thus controlled by the relative magnitudes of the exchange current density of the different species involved. These facts establish that oscillations in such systems are caused by the periodic concentration change of bromine and bromide ion.

Acknowledgements

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