

ANOMALOUS BEHAVIOUR OF PLATINUM ELECTRODE IN BRIGGS-RAUSCHER OSCILLATING CHEMICAL REACTION

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ABSTRACT

Platinum electrode when given anodic or cathodic treatment show attenuation in potential oscillations in the study of Briggs - Rauscher oscillating chemical reaction. Moreover, some electrodes did not even indicate oscillations though the solution was oscillating. Further it was observed that keeping an electrode in Hydrogen peroxide for a number of days rejuvenates its capacity to sense oscillations. Mechanism of such behavior is contemplated.

Key Words : Briggs - Rauscher, Oscillating reaction, Anomalous behaviour, Hydrogen peroxide and Platinum electrode.

INTRODUCTION

Study of oscillating chemical reactions and chemical chaos has gained considerable importance of late¹⁻⁴. Further these systems are very sensitive of experimental parameters such as stirring, mixing and temperature etc²⁻⁴. So one needs to be caution in interpreting and ascertaining the data obtained from various kinds of sensors. Oscillating chemical reactions are being studied generally by spectrophotometry⁶ and by potentiometric techniques⁷.

Platinum electrode and some ion selective electrodes are the most common indicator electrodes being used in potentiometric studies⁷. The quantitative behaviour of ion selective electrodes has been thoroughly investigated^{8,9}. The use of platinum electrode is rather widespread; however the quantitative use of its potentiometric data is rather poorly defined¹⁰, through an identification of species responsible for oscillation could be achieved by an examination of exchange current densities^{11,15}.

The present study brings out an anomalous behaviour of platinum electrode in the Briggs-Rauscher (BR) oscillating chemicals reaction.

EXPERIMENTAL

The reaction system studied contained Potassium iodate, Sulfuric acid, Manganous sulfate,

Malonic acid/Acetone and Hydrogen peroxide as component constituents.

This Oscillating chemical is known as the Briggs-Rauscher reaction. The chemicals used were of AR grade. Water used for all preparations was double distilled, the second distillation being from permanganate solution.

Smooth, bright Platinum foils and wire electrodes of different sizes were employed. Saturated calomel was used as the reference electrode together with a salt bridge consisting of 10% potassium nitrate solution.

Total volume of the solution was 100 ml. The reaction mixture except hydrogen peroxide was kept well stirred in a glass cell with an outer jacket through which pre-conditioned water could be circulated so as to maintain the required temperature.

When the temperature of the reaction mixture became constant within $\pm 0.10^\circ\text{C}$ of the required value, hydrogen peroxide solution maintained at the same temperature was instantly transferred.

RESULTS AND DISCUSSION

Fig 1. Present traces of a platinum electrode with maximum sensitivity for the BR systems at different initial compositions with malonic acid as the organic substrate at 35°C It can be noted that

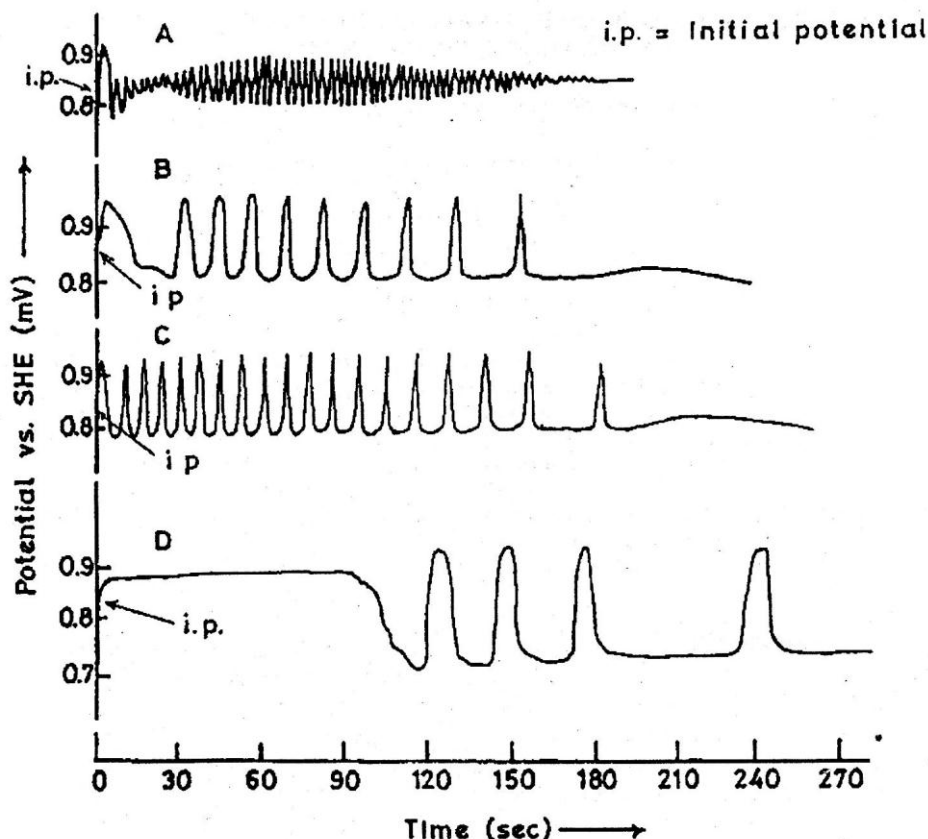


Fig. 1 Platinum electrode (maximum sensitivity) traces at different initial compositions for the B-R reaction

- A. $[\text{KIO}_3] = 0.05\text{M}$, $[\text{H}_2\text{SO}_4] = 0.025\text{M}$, $[\text{MA}] = 0.175\text{M}$, $[\text{MnSO}_4] = 0.005\text{M}$, $[\text{H}_2\text{O}_2] = 1.0\text{M}$
 B. $[\text{KIO}_3] = 0.05\text{M}$, $[\text{H}_2\text{SO}_4] = 0.075\text{M}$, $[\text{MA}] = 0.05\text{M}$, $[\text{MnSO}_4] = 0.005\text{M}$, $[\text{H}_2\text{O}_2] = 1.0\text{M}$
 C. $[\text{KIO}_3] = 0.1\text{M}$, $[\text{H}_2\text{SO}_4] = 0.025\text{M}$, $[\text{MA}] = 0.05\text{M}$, $[\text{MnSO}_4] = 0.005\text{M}$, $[\text{H}_2\text{O}_2] = 1.0\text{M}$
 D. $[\text{KIO}_3] = 0.05\text{M}$, $[\text{H}_2\text{SO}_4] = 0.025\text{M}$, $[\text{MA}] = 0.175\text{M}$, $[\text{MnSO}_4] = 0.005\text{M}$, $[\text{H}_2\text{O}_2] = 0.25\text{M}$

the initial potential is in neighborhood about 0.8V (Vs SHE) and that the potential oscillations are of the order of 100mV and above. When these electrodes were given anodic or cathodic treatment (In 0.10 M H_2SO_4 acid, using another platinum electrode as counter electrode, with evolution of oxygen or hydrogen on the electrode surface), we were surprised to see that there is attenuation in the amplitude of the potential oscillations observed as shown in Fig. 2. The base potential is nearly the same, whereas, the upper potential has decreased. Further, there is a shift of the initial potential (before the addition of the hydrogen peroxide) to the positive direction. When the duration of the anodic

or cathodic treatment was increased it was observed that the shift of the initial potential is greater in the positive directions and the electrode is more insensitive and potential oscillations are further attenuated. It was moreover, observed that, the electrode, with was given anodic or cathodic treatment, when dipped in a test tube containing hydrogen peroxide, and initiated vigorous disproportion of hydrogen peroxide. The hydrogen peroxide thus decomposed was replenished by fresh additions. When this was done it was note that the ability of the electrode to decompose hydrogen peroxide decreased. When the electrode was kept in such a solution for a number of days its

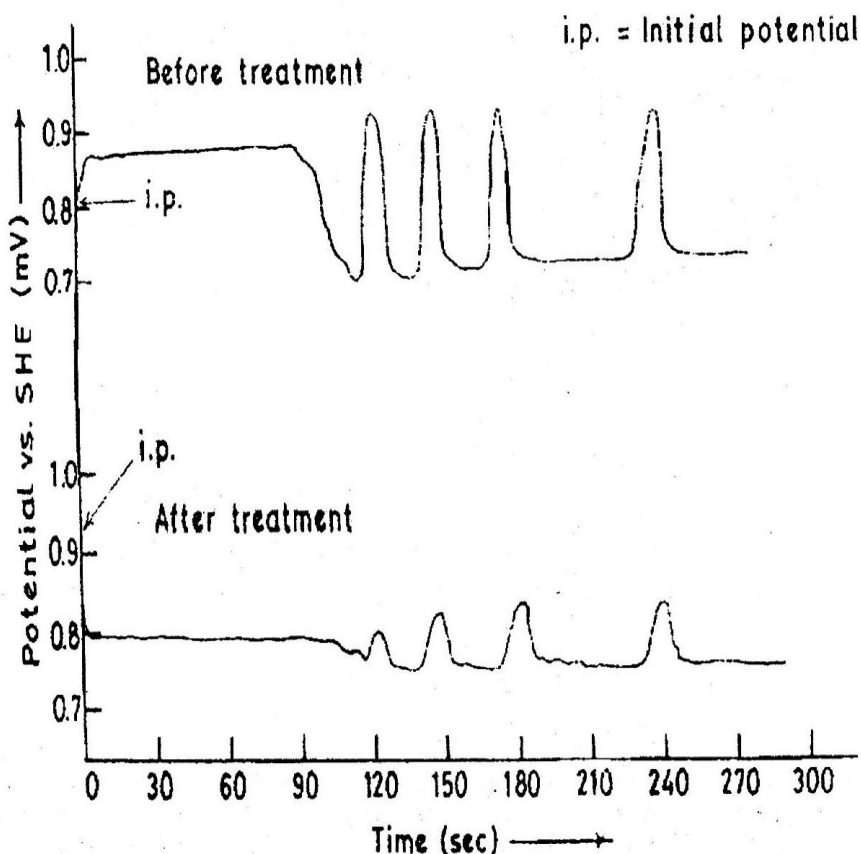


Fig. 2 Platinum electrode traces before and after anodic/cathodic treatment in B-R reaction containing Malonic acid as the organic substrate Initial Composition. $[KI\ O_3] = 0.05M$, $[H_2S\ O_4] = 0.025M$, $[MA]=0.05M$, $[MnSO_4]= 0.005M$, $[H_2O_2]=0.025M$

capacity to sense oscillations rejuvenated. Similar behaviour for the observed when Malonic acid was replaced by acetone. Fig.3 presents such behaviour for the electrode studied in Fig 2. when, Malonic acid is replaced by Acetone.

Platinum is very good catalyst for the decomposition of hydrogen peroxide¹³ an electrode with anodic or cathodic treatment decompose hydrogen peroxide vigorously. In principle, the response of a electrode in a system containing various redox couples would depend not only on the concentrations of the oxidized and reduced species present on the electrode but also on the exchange current densities, the more reversible the electrode is to that couple which has the highest exchange current density¹⁴. So platinum should largely sense the iodine-iodide couple as it

is one of the redox couples having the highest exchange current density¹⁵ in the BR reaction.

This is the story, if the electrode is inert. However, if it is not inert then what? The behavior describes above indeed represented a situation where the electrode is not inert. The probable reason for the inventively is due to the adsorption of highly active layer of oxygen or hydrogen which reacts with hydrogen peroxide resulting in an entirely different structure at the double layer. So one has to be careful while analyzing the potentiometric data of platinum electrode. As far as possible use of platinum electrode should be avoided where its catalytic activity interferes with the equilibrium electrochemical measurement of the system. Further studies in other oscillating system containing hydrogen peroxide is in progress.

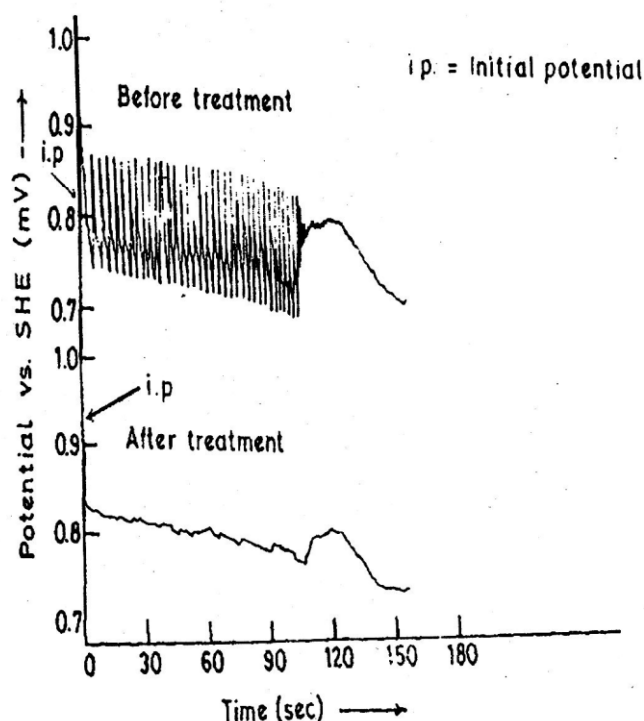


Fig. 3 Platinum electrode traces before and after anodic/cathodic treatment in B-R reaction containing acetone as the organic substrate Initial Composition. $[KIO_3] = 0.02M$, $[H_2SO_4] = 0.08M$, $[(CH_3)_2CO] = 2M$, $[MnSO_4] = 0.005M$, $[H_2O_2] = 1.0 M$

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